MERCURY

ANNUAL SURVEY COVERING THE YEAR 1977

DIETMAR SEYFERTH

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139 (USA)

TABLE OF CONTENTS

Mercury, Annual Survey covering the year 1976, see J. Organometallic Chem., 143 (1977) 153-308.

1. REVIEWS AND BOOKS

"The Chemistry of Mercury", a 288 page book edited by C.A. McAuliffe (1), contains an excellent chapter by A.J. Bloodworth on organomercury compounds. In addition, there are chapters devoted to the history of mercury and its compounds, the structural inorganic chemistry of mercury and the biochemistry and toxicology of mercury and its compounds. For a review of this book, see (2).

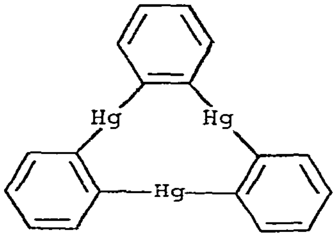
A review on the chemistry of α-nitro-organoelement compounds covers $O_2N-C-Hg$ type compounds (3); the utilization of halomethyl- and α-haloalkylmercurials as divalent carbon transfer agents was reviewed by Nefedov, D'yachenko and Prokof'ev (4).

2. PREPARATION OF ORGANOMERCURY COMPOUNDS

A. Reactions of Elemental Mercury and Amalgams

The reaction of elemental mercury with pentfluorobenze in antimony pentafluoride solution at 70°C gave $(C_6F_5)_2Hg$ i 30% yield (5). It is believed that this reaction proceeds with initial oxidation of elemental mercury by SbF_5 to give Hg_3^{2+} (Gillespie, 1973) and that the latter is the active mercurating species.

A reexamination of the reactions of 1,2-dihalobenzenes sodium amalgam has been carried out by Massey and his cowork (6). In all experiments, the isolated product was the ortho phenylenemercury trimer, 1. In some cases, ortho-terphenylenemercury dimer, $(C_6H_4C_6H_4C_6H_4Hg)_2$, was a by-product. No evidence for the previously reported (Wittig, 1958) ortho-phenylenemercury hexamer was obtained. The action of sodiu amalgam on 2,2'-diiodobiphenyl in THF gave no organomercury products.



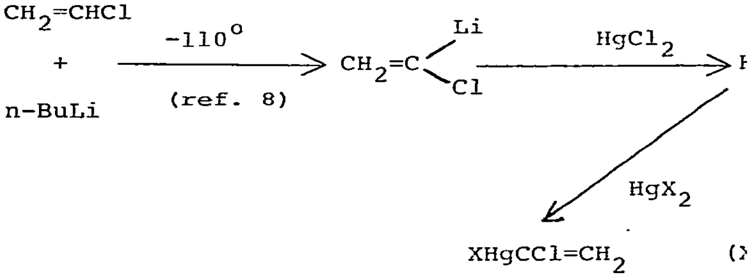
1

B. Reactions of Organometallic Reagents with Hg(II) Derivatives

The reaction of 2,2'-dilithiobiphenyl with mercuric chloride in diethyl ether gave ortho-biphenylenemercury, whic was claimed, on the basis on mass spectrometry, to be a trime rather than a tetramer as reported previously (Wittig, 1954)

Other examples of the organolithium synthesis of mercuria may be cited, and some of the more striking examples are give below.

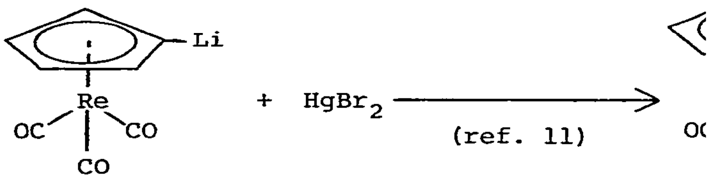
$$Li(CCl_2CHCH_2) + HgCl_2 \xrightarrow[\text{(ref. 7)}]{} ClHg$$

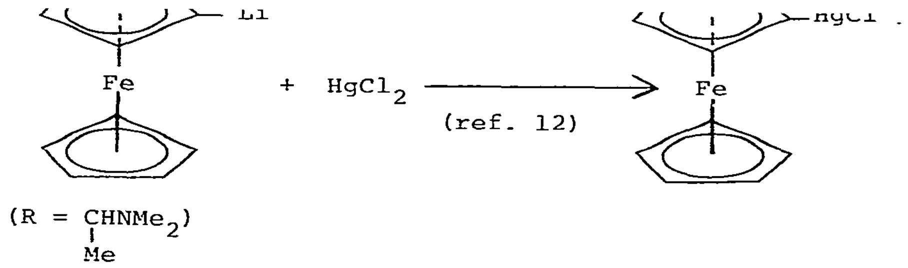


$$2\ (PhS)_2CHLi + HgBr_2 \xrightarrow[\text{(ref. 9)}]{} Hg[CH($$

$$(PhS)_2CHLi + PhHgCl \xrightarrow[\text{(ref. 9)}]{} PhHgCH($$

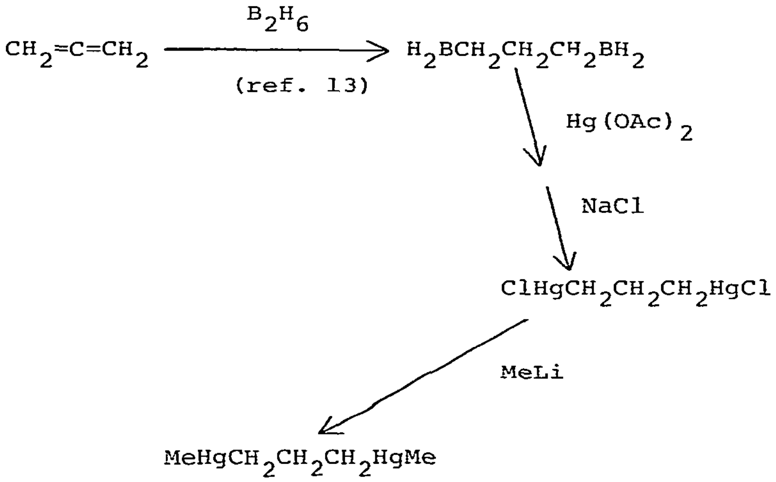
$$(Me_3Si)_3CLi + MeHgBr \xrightarrow[\text{(ref. 10)}]{} Me$$



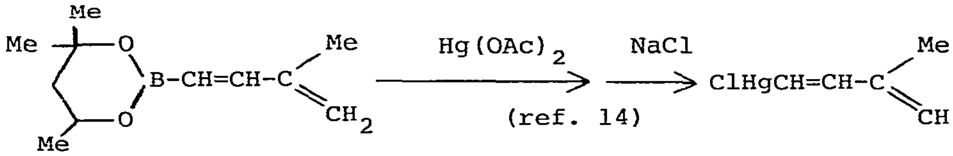


Organoboron compounds and organic derivatives of the Gro IV elements also transfer groups to mercury.

Boron



$$\mathrm{Me_2C{=}C{=}CHB(OMe)_2} \xrightarrow[\text{(ref. 14)}]{\mathrm{Hg(OAc)_2}} \xrightarrow{\mathrm{NaCl}} \mathrm{Me_2C{=}C{=}CHHgCl}$$



$$\begin{tikzcd} NaBPh_4 + {}^{203}HgCl_2 \arrow[r, "H_2O", "(ref.\ 15)"'] & {}^{203}HgPh_2 \arrow[d, "{}^{203}HgCl_2"] \\ & Ph^{203}HgCl \end{tikzcd}$$

Silicon

$$PhSiX_3 + HgY_2 \xrightarrow[(ref.\ 16)]{} PhHgY$$

$(X = F, Cl, OMe, OEt, OAc;\ \ Y = Cl, Br, I, CN, OAc, OBz)$

Cleavage of $PhSiF_3$ was the most facile, occurring at 25° with mercuric acetate and mercuric cyanide, at 60-65° with mercuric halides and phenylmercuric acetate. With mercuric oxide, the following reaction takes place:

$$2\ PhSiF_3 + HgO_{(s)} \xrightarrow{benzene} Ph_2Hg + (F_3Si)_2O$$

Tin

$$Et_2SnAr_2 + 2\ Hg(OAc)_2 \xrightarrow[(ref.\ 17)]{} 2\ ArHgOAc + Et_2Sn(OAc)_2$$

$$Et_2SnAr'_2 + 2\ ArHgOAc \xrightarrow[(ref.\ 17)]{} 2\ ArHgAr' + Et_2Sn(OAc)_2$$

$(Ar, Ar' = Ph,\ p\text{-}MeC_6H_4,\ p\text{-}ClC_6H_4,\ 1\text{-}C_{10}H_7)$

$$R_3SnO_2CR' + HgCl_2 \xrightarrow[(ref.\ 18)]{H_2O} RHgCl$$

$$Ph_3SnO_2CR \quad + \quad Hg(OAc)_2 \xrightarrow[\text{(ref. 18)}]{H_2O} Ph_2Hg$$

$$Et_4Sn \quad + \quad Hg(O_2CR)_2 \xrightarrow[\text{(ref. 19)}]{} EtHgO_2CR \quad + \quad Et_3SnO_2CR$$

(A rate study, with R = Me, Et, t-Bu, $ClCH_2$, $MeOCH_2$, $ClCH_2CH_2$. It was concluded that eletrophilic attack by the mercuric carboxylate on tetraethyltin is the dominant process.)

The cleavage of transition metal-alkyl or -aryl σ bonds by HgX_2 has been of recent interest from the point of view of mechanism, but such reactions usually offer no preparative advantages. New examples include a kinetics and mechanism study of Fe-C cleavage (20):

$$CpFe(CO)_2R \quad + \quad HgX_2 \longrightarrow CpFe(CO)_2X \quad + \quad RHgX$$

(Here R = primary alkyl, aryl; X = Cl, Br, I)

With secondary, tertiary, allylic and benzylic iron derivatives another mode of reaction was observed:

$$CpFe(CO)_2R \quad + \quad HgX_2 \longrightarrow CpFe(CO)_2HgX \quad + \quad RX$$

Cobalt-carbon bond cleavage (kinetics and mechanism) by Hg(II) was studied by two groups:

$$(H_2O)Co(dmgH)_2(CH_2)_4Co(dmgH)_2(H_2O) \quad + \quad Hg^{2+}_{aq} \xrightarrow[\text{(ref. 21)}]{}$$

$$\begin{tikzcd} (H_2O)(dmgH)_2Co(CH_2)_4Hg^+ \arrow[d, "Hg^{2+}_{aq}"] \\ {}^+HgCH_2CH_2CH_2CH_2Hg^+ \end{tikzcd}$$

The intricacies of methyl group cleavage from methylcobalamin by Hg(II) in aqueous media were studied by means of stopped-flow techniques (22).

C. Extrusion Reactions

Decarboxylation, desulfination and desulfonation of Hg(II) carboxylates, sulfinates and sulfonates, respectively, i.e., extrusion of carbon dioxide, sulfur dioxide and sulfur trioxide, has found occasional use in organomercurial synthesis. Thermal decarboxylation is particularly valuable in the preparation of polyhaloarylmercurials. Deacon and his coworkers (23) have used this procedure in the synthesis of polybromophenylmercury compounds:

$$(XC_6Br_4CO_2)_2Hg \xrightarrow{\text{pyridine}} (XC_6Br_4)_2Hg \quad + \quad 2\ CO_2$$

(X = Br, p-F, p-Cl, p-MeO)

$$C_6H_5HgO_2CC_6Br_5 \xrightarrow{\text{pyridine}} C_6H_5HgC_6Br_5 \quad + CO_2$$

$$(p\text{-}MeC_6Br_4CO_2)_2Hg \xrightarrow{\text{pyridine/nitrobenzene}} (p\text{-}MeC_6Br_4)_2Hg + 2\ CO_2$$

$$(o\text{-}MeC_6Br_4CO_2)_2Hg \xrightarrow[Hg(O_2CCF_3)_2]{\text{molten}} \xrightarrow{\text{NaCl}} o\text{-}MeC_6Br_4HgCl$$

also:

$$(C_6Br_5)_2Hg \quad + \quad HgX_2 \longrightarrow 2\ C_6Br_5HgX \qquad (X = Cl,\ Br)$$

Perbromodiphenylmercury shows remarkable thermal stability: it can be heated to 400°C without decomposition.

The mercury(II) o- and m-carborane-1-carboxylates 2 and 3 have been prepared (24). The uncomplexed Hg(II) o-carborane-

$[B_{10}H_{10}(HC_2CO_2)]_2Hg \cdot 2L$ (L = phen·H_2O, bipy, Ph_3P, py)

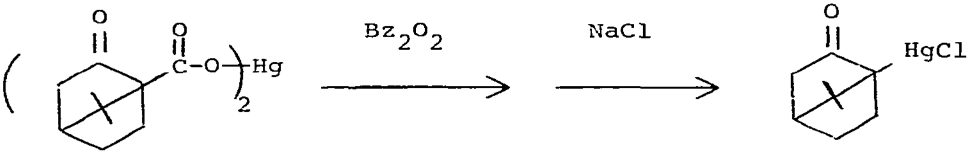
2

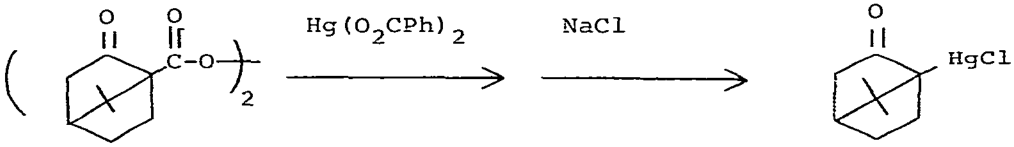
$[HC(B_{10}H_{10})CCO_2]_2Hg \cdot 2L$ (L = phen·H_2O)

3

1-carboxylate decomposed at room temperature to Hg(I) salts, but the *m* isomer was stable. Complexes 2 and 3 decarboxylated when heated above their melting points, giving the corresponding biscarboranylmercury derivatives.

The decarboxylation processes shown below proceeded with racemization of the optically active starting materials (25):

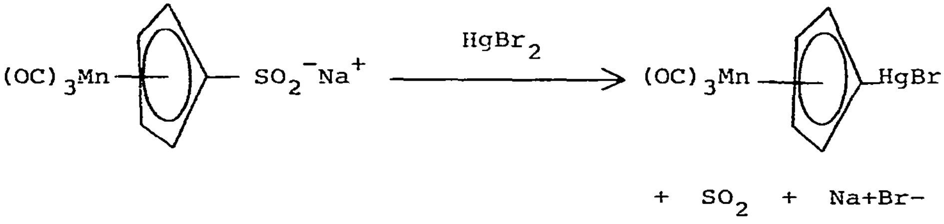




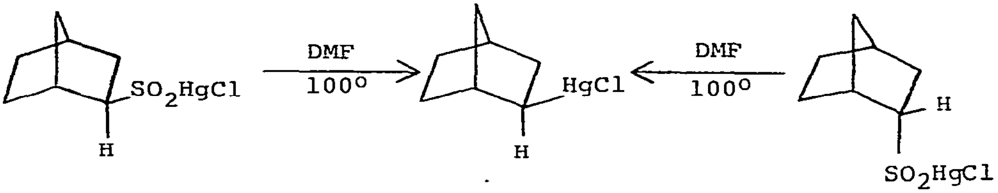
This is in line with the known radical mechanism of such processes. Of interest also is a spectroscopic study of the photolytic decarboxylation of mercuric trifluoroacetate (26). Upon UV irradiation, this compound decomposes to give trifluoromethyl radicals. At room temperature these combine to produce C_2F_6, but at -196°C, bis(trifluoromethyl)mercury is formed:

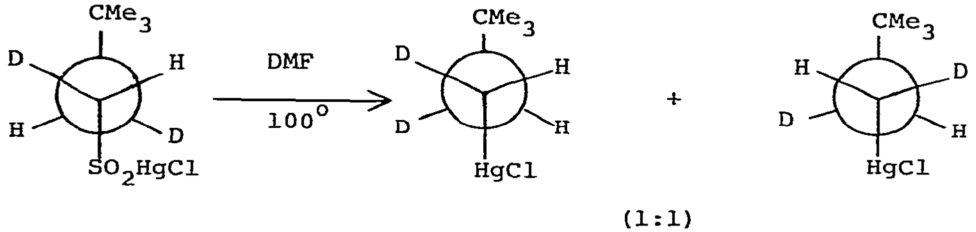
$$\begin{tikzcd}
Hg(O_2CCF_3)_2 \arrow[rr, "h\nu,\ -196^{\circ}"] & & CO_2 + \cdot CF_3 + \cdot HgO_2CCF_3 \arrow[d, "h\nu,\ -196^{\circ}"] \\
& & CF_3HgO_2CCF_3 \arrow[dl, "h\nu"'] \\
& CO_2 + \cdot CF_3 + \cdot HgCF_3 \arrow[dr] & \\
& & (CF_3)_2Hg
\end{tikzcd}$$

A synthetic application of the SO_2 extrusion reaction has been reported from the metallocene series (27):



The stereochemistry of such SO_2 extrusion processes (Peters reaction) has been studied (28):





Since the products were found to be stable to the reaction conditions in control experiments, sulfur dioxide extrusion must proceed via a stereochemically labile intermediate. Free radical intermediates could not be implicated and the mechanism remains unknown.

D. Electrochemical Procedures

Anodic oxidation of carboxylic acids serves in the preparation of $Hg_2(O_2CR)_2$, and in the same study it was found that decarboxylation of mercury(II) carboxylates could be initiated electrolytically (29). Thus, electrolysis of a solution of mercuric acetate in acetic acid containing potassium acetate at 100^0 in a cell with graphite electrodes at 0.5 amp and 18V gave methylmercury(II) products in yields up to 47%. Mercury(I) acetate was formed as a by-product.

Electrolysis of 1-iododecane in DMF with $R_4N^+ClO_4^-$ supporting electrolyte, using a mercury cathode and potentials more positive than the polarographic maximum, gave di-n-decylmercury in substantial yield (30). Of interest is the purification of this product by gel permeation chromatography. The following scheme was suggested:

$$RCH_2I \quad + \quad e^- \longrightarrow RCH_2\cdot \quad + \quad I^-$$

$$RCH_2\cdot \longrightarrow RCH_2\cdot(ads)$$

$$RCH_2\cdot(ads) \quad + \quad Hg \longrightarrow RCH_2Hg\cdot(ads)$$

$$2\ RCH_2Hg\cdot(ads) \longrightarrow (RCH_2)_2Hg \quad + \quad Hg$$

Similar electrolytic reduction of 1,4- and 1,5-dibromoalkanes using a mercury cathode (low cathode potentials, aprotic media) gave solid products which were believed to be organomercury polymers of type 4 (31).

$$-\!\!\left[\, Hg(CH_2)_n\text{-}Hg\text{-}(CH_2)_n \,\right]\!\!-_x$$

E. Photochemical Procedures

Photolysis of aliphatic amino acids of type $RCH(NH_2)CO_2H$ ($R = Me$, Me_2CH, Me_2CHCH_2, Me_3C) in aqueous medium in the presence of mercuric chloride gave methylmercury(II) species (32). Presumably, photofragmentation of the amino acids gives methyl radicals which then react with Hg(II). The environmental implications of such processes are obvious.

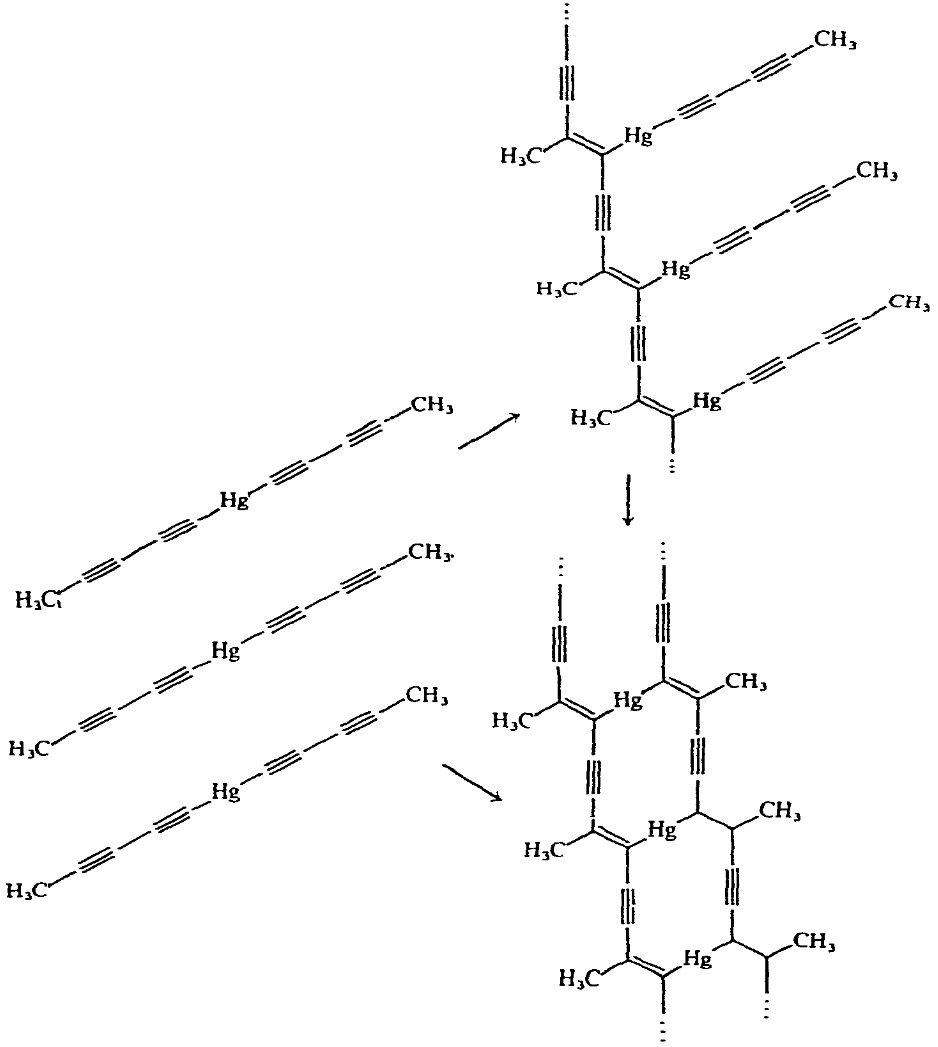
More work has been published on the photochemical transformation of mercuric sulfide in aqueous medium containing acetic acid to methylmercury(II) (33).

F. Miscellaneous Procedures

Bis(1,3-pentadiynyl)mercury has been prepared (34):

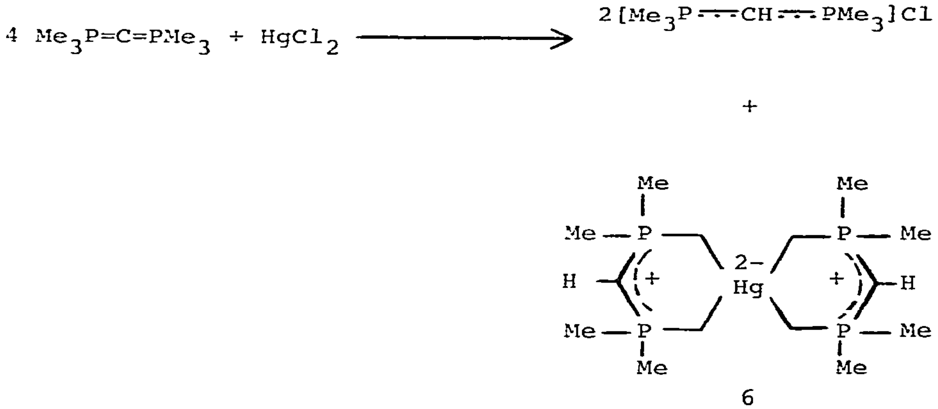
$$2\ \mathrm{MeC{\equiv}C{-}C{\equiv}CH} + \mathrm{HgI_2} + 2\mathrm{KI} + 2\mathrm{KOH} \longrightarrow (\mathrm{MeC{\equiv}C{-}C{\equiv}C})_2\mathrm{Hg} + 4\mathrm{KI} + 2\mathrm{H_2O}$$

UV or thermally induced polymerization of this compound gave a ladder polymer, 5.



5

The first tetraalkylmercurate(II) compound, 6, has been prepared (35):



6

3. USE OF ORGANOMERCURY COMPOUNDS IN SYNTHESIS

A. Synthesis of Organometallic Compounds

1. Reactions of Mercurials with Elements

Full details have been provided concerning the synthesis of perfluorophenylytterbium compounds by the mercurial route (36):

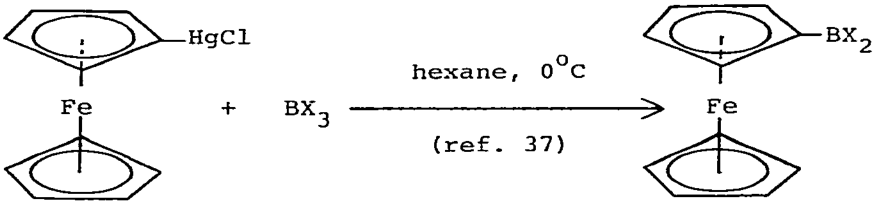
$$(C_6F_5)_2Hg \quad + \quad Yb \xrightarrow[\text{room temp.}]{\text{THF}} (C_6F_5)_2Yb\cdot 4THF$$

Propane-1,3-di(magnesium bromide) has been prepared in solution by the mercury displacement reaction in the presence of magnesium bromide (13):

$$MeHgCH_2CH_2HgMe + Mg \quad + \quad MgBr_2 \xrightarrow{\text{THF}} BrMgCH_2CH_2CH_2MgBr$$

2. Reactions of Mercurials with Element Halides and Hydrides

The equations below summarize new examples of this long established procedure.



$$Hg(CN)_2 + Et_3SiCl \xrightarrow[\text{(ref. 38)}]{\text{DME}} 2\ Et_3SiCN + HgCl_2$$

$$Hg(O_2CR)_2 + 2\ Et_3SiX \xrightarrow[\text{(ref. 38)}]{} 2\ Et_3SiO_2CR + HgX_2$$

(X = Cl, Br, I)

Glockling and Sweeney have investigated the use of mercurials for partial alkylation of Group IV tetrahalides (39). A selection of their results is given below.

$$2\ Me_2Hg + SnCl_4 \xrightarrow{80^\circ,\ 2h} Me_2SnCl_2$$

$$Me_2Hg + SnCl_4 \xrightarrow{20^\circ,\quad 2\ min} MeSnCl_3$$

$$4\ Me_2Hg + SnCl_4 \xrightarrow{130^\circ,\ 8h} Me_3SnCl$$

Similar reactions were carried out with $SnBr_4$ and SnI_4.

$$Me_2Hg + GeX_4 \xrightarrow{110\text{-}150^\circ} MeGeX_3$$

(X = Cl, Br)

$$Me_2Hg + SiI_4 \xrightarrow{100^\circ,\ 3d} MeSiI_3 + Me_2SiI_2$$

In similar fashion, $Me_3SiCH_2GeX_3$ (X = Cl, Br), $Me_3SiCH_2SnX_3$

(X = Cl, Br, I) and $(Me_3SiCH_2)_2SiX_2$ (X = Cl, Br, I) were prepared by appropriate reactions of $(Me_3SiCH_2)_2Hg$. Similar preparations were carried out with $(Me_3GeCH_2)_2Hg$.

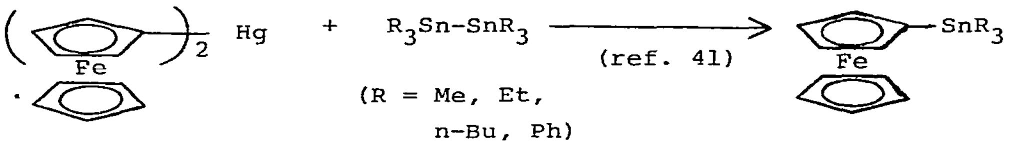
Other examples of mercurial-based organogermanium and organotin preparations were reported:

$$(CF_3)_2Hg + GeBr_4 \xrightarrow[\text{(ref. 40)}]{110^{o}} CF_3GeBr_3\ (55\%) + (CF_3)_2GeBr_2\ (22\%) + (CF_3)_3GeBr\ (18\%) + (CF_3)_4Ge\ (4\%)$$

A reaction at 150°, 2 $(CF_3)_2Hg + GeBr_4$, gave $(CF_3)_2GeBr_2$ (10%), $(CF_3)_3GeBr$ (65%) and $(CF_3)_4Ge$ (20%).

$$(CF_3)_2Hg + SnBr_4 \xrightarrow[\text{(ref. 40)}]{125^{o},\ 67h} CF_3SnBr_3\ (54\%) + (CF_3)_2SnBr_2\ (19\%)$$

No trifluoromethyl-silicon bromides were produced when $(CF_3)_2Hg$ was heated with silicon tetrabromide.



Mercury reagents also have found application in the synthesis of organic derivatives of Group V elements and of tellurium.

$$ICH_2HgI + F_2PI \xrightarrow[\text{(ref. 42)}]{Hg} F_2PCH_2I + HgI_2$$

$$5\ MePH_2 + 5\ (PhCH_2)_2Hg \xrightarrow[\text{(ref. 42)}]{} \text{cyclo-}(MeP)_5 + 10PhMe + 5\ Hg$$

$$5\ RAsH_2 + 5\ (PhCH_2)_2Hg \longrightarrow \text{cyclo-}(RAs)_5 + 10PhMe + 5Hg$$

(R = Me, Et)

$$MeSbH_2 + (PhCH_2)_2Hg \longrightarrow 1/x \ (MeSb)_x + 2\ PhMe + Hg$$

$$Me_2AsH + (PhCH_2)_2Hg \longrightarrow Me_2AsAsMe_2 + Me_2AsCH_2Ph$$

$$MeMCl_2 + (PhCH_2)_2Hg \longrightarrow Me(Cl)MCH_2Ph + PhCH_2HgCl$$

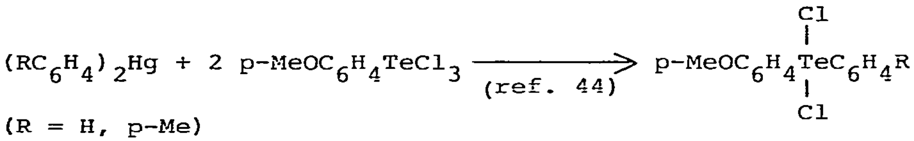
(M = P, As)

$$MeAsI_2 + (PhCH_2)_2Hg \longrightarrow MeAs(CH_2Ph)_2 + HgI_2$$

$$2\ Me_2AsI + (PhCH_2)_2Hg \longrightarrow 2\ Me_2AsCH_2Ph + HgI_2$$

$$(RC_6H_4)_2Hg + TeCl_4 \xrightarrow[\text{(ref. 44)}]{} (RC_6H_4)_2TeCl_2$$

(R = p-MeO, p-Me, H, p-Br)



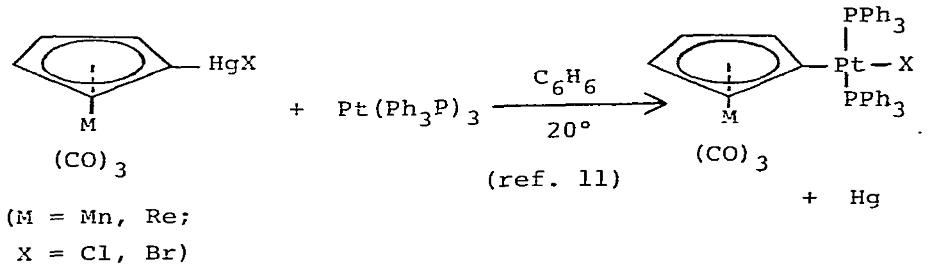
$$(RC_6H_4)_2Hg + 2\ p\text{-}MeOC_6H_4TeCl_3 \xrightarrow[\text{(ref. 44)}]{} p\text{-}MeOC_6H_4\underset{\displaystyle Cl}{\overset{\displaystyle Cl}{Te}}C_6H_4R$$

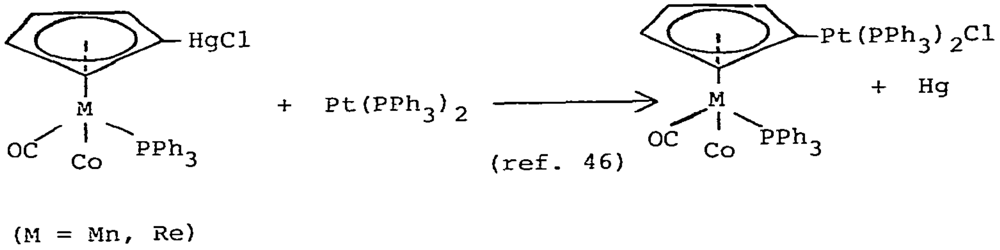
(R = H, p-Me)

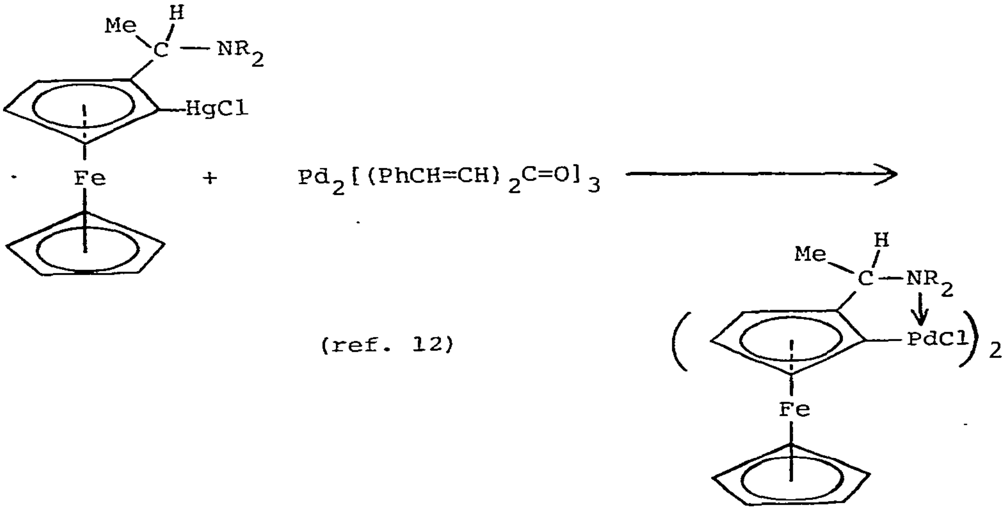
Organomercurials also have played a role in synthetic transition metal organic chemistry.

$$Ph_2Hg + Au(CO)Cl \xrightarrow[\text{(ref. 45)}]{} Ph_2AuHgCl$$

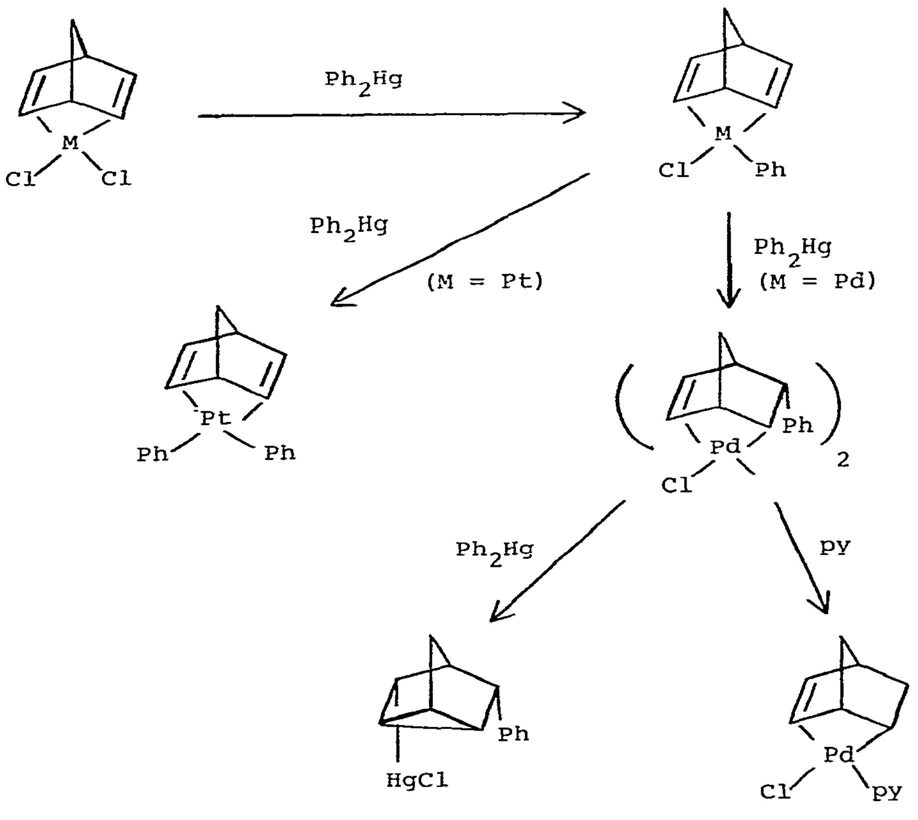
(The product of this reaction, when dry, explodes violently, giving biphenyl, metallic gold and phenylmercuric chloride).



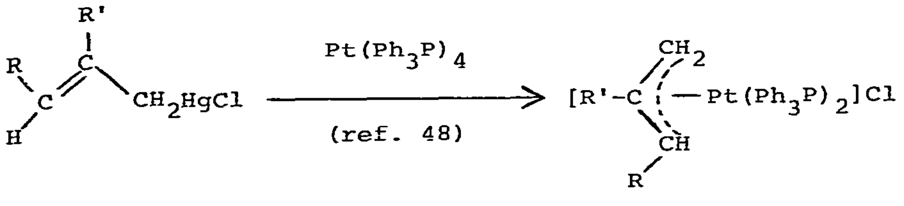




Maitlis and his coworkers have studied reactions of diphenylmercury with norbornadiene complexes of platinum and palladium (II) chlorides and related complexes (47).



Allylic mercurials have found further application as well (48)



(R,R' = H,H; H,Me
H,Ph; Me,H
Ph,H; Ac,Me)

but:

$$K[PtCl_3(CH_2{=}CH_2)] + 2\ CH_2{=}CHCH_2HgCl \xrightarrow{MeOH} CH_2{=}CHCH_2CH_2CH{=}CH_2 + Pt + 2\ HgCl_2 + KCl + C_2H_4$$

B. Applications in Organic Synthesis

1. Halogenolysis and Related Processes

Halogenolysis of the C-Hg bond has found useful applications in the synthesis of organic halides. Deacon and Farquharson have reported the synthesis of polyhaloaromatic compounds by this procedure:

$$(p\text{-}ZC_6Br_4)_2Hg \quad + \quad I_2\ (\text{or } I_3^-) \xrightarrow[\text{(ref. 23)}]{DMF} p\text{-}ZC_6Br_4I$$

(Z = F, Cl, Br, Me, OMe)

$$ZC_6Br_4HgCl \quad + \quad I_2\ (\text{or } I_3^-) \xrightarrow[\text{(ref. 23)}]{DMF} ZC_6Br_4I$$

(Z = o-Me, m-OMe)

$$ZC_6(HgO_2CCF_3)_5 + 5\ Br_3^- \xrightarrow[\text{(ref. 49)}]{} ZC_6Br_5 + 5HgBr_2 + 5\ CF_3CO_2^-$$

(Z = o, m, p-Me, F, Cl, Br, MeO, NO_2, CF_3, H)

$$ZC_6(HgO_2CCF_3)_4CO_2H + 4\ Br_3^- \xrightarrow[\text{(ref. 49)}]{H_2O} ZC_6Br_4CO_2H + HgBr_2 + 4\ CF_3CO_2^-$$

(Z = as above)

$$ZC_6(HgO_2CCF_3)_5 \quad + \quad 5\ I_3^- \xrightarrow[\text{(ref. 50)}]{\text{DMF, r.t.}} ZC_6I_5$$

$$ZC_6(HgO_2CCF_3)_5 + 5\ Cl_2 \xrightarrow[\text{(ref. 50)}]{\text{DMF, r.t.}} ZC_6Cl_5$$

The permercurated arenes were obtained by the permercuration of the respective substituted arene with mercuric trifluoroacetate at high temperature. The results of the study of ref. 50 are given in Table 1.

Table 1. Preparations of permercurated arenes, and conversions into periodo- and perchloro-arenes

Arene	$Hg(O_2CCF_3)_2$ mol per mol arene	Temp. (°C)	Polymercurated arene	Polyiodo-arene(a)	Yield (%)	Polychloro-arene(b)	Yield (%)
$C_6H_5NO_2$	7	240	$C_6(HgO_2CCF_3)_5NO_2$	$C_6I_5NO_2$	50	$C_6Cl_5NO_2$	68
C_6H_5HgCl	15	200	$C_6(HgO_2CCF_3)_6$	C_6I_6	55	C_6Cl_6	56
C_6H_5HgCl	7	180	$C_6H(HgO_2CCF_3)_5$ $+ C_6(HgO_2CCF_3)_6$	C_6HI_5 $+ C_6I_6$	51 7	C_6HCl_5 $+ C_6Cl_6$	41 16
C_6H_5Br	7	180	$C_6(HgO_2CCF_3)_5Br$	C_6I_5Br	55	C_6Cl_5Br	46
$o\text{-}BrC_6H_4CO_2H$	12	230	$C_6(HgO_2CCF_3)_5Br$	C_6I_5Br	40	C_6Cl_5Br	
$o\text{-}ClC_6H_4CO_2H$	8	225	$C_6(HgO_2CCF_3)_5Cl$	C_6I_5Cl	66		
$o\text{-}FC_6H_4CO_2H$	7	215	$C_6(HgO_2CCF_3)_5F$	C_6I_5F	42	C_6Cl_5F	40
$o\text{-}FC_6H_4CO_2H$	15	225	$C_6(HgO_2CCF_3)_5F$	C_6I_5F	40		
$o\text{-}CF_3C_6H_4CO_2H$	7	245	$C_6(HgO_2CCF_3)_5CF_3$	$C_6I_5CF_3$	45		
$o\text{-}CF_3C_6H_4CO_2H$	15	245	$C_6(HgO_2CCF_3)_5CF_3$	$C_6I_5CF_3$	15		
$p\text{-}CH_3OC_6H_4CO_2H$	7	180	$C_6(HgO_2CCF_3)_5OCH_3$	$C_6I_5OCH_3$	61	$C_6Cl_5OCH_3$	61
$C_6H_5CO_2Na$	8	200	$C_6(HgO_2CCF_3)_5CO_2Na$ $+ C_6(HgO_2CCF_3)_6$	$C_6I_5CO_2H$ $+ C_6I_6$	26 44		
$C_6H_5CO_2Na$	7	180	$C_6(HgO_2CCF_3)_5CO_2Na$ $+ C_6(HgO_2CCF_3)_6$			$C_6Cl_5CO_2H$ $+ C_6Cl_6$	50 11
$p\text{-}CH_3C_6H_4SO_2Na$	7	180	$C_6(HgO_2CCF_3)_5CH_3$	$C_6I_5CH_3$	40	$C_6Cl_5CH_3$	46
Naphthalene	16	180	$C_{10}(HgO_2CCF_3)_8$ $+ C_{10}H(HgO_2CCF_3)_7$			$C_{10}Cl_8$ $+ C_{10}HCl_7$	46 9

a) Obtained after cleavage of $C_6(HgO_2CCF_3)_5X$ with sodium triiodide in dimethylformamide at room temperature for 3 days ($X = CH_3$ or OCH_3), 7 days (X = H or Br), or 14 days (other examples).

b) Obtained after cleavage of $C_6(HgO_2CCF_3)_5X$ with chlorine in dimethylformamide at room temperature for 3 h except when X = OMe where the reaction time was 8 h.

The cleavage of diarylmercurials, ArHg, with Ar = Ph, p-MeC_6H_4, p-FC_6H_4, with bromine trifluoride in the presence of $BF_3 \cdot OEt_2$ at around -40°C proceeded as shown, giving the respective diarylbromonium salts (51):

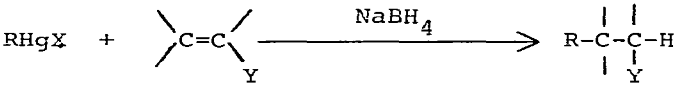
$$2\ Ar_2Hg + BrF_3 + 3\ BF_3 \cdot OEt_2 \longrightarrow [Ar_2Br][BF_4] + 2\ ArHgBF_4$$

2. Radical Transfer Reactions

The reduction of organomercuric halides and carboxylates with sodium borohydride has been shown to be a process which involves radical intermediates. (See previous Annual Surveys of Organomercury Chemistry.)

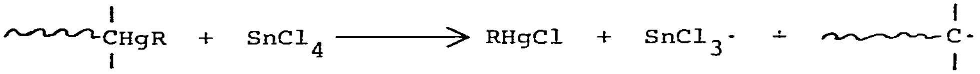
$$\begin{tikzcd}
RHgX \arrow[r, "NaBH_4"] & RHgH \arrow[r] & RHg\cdot \arrow[d] & + & H\cdot \\
 & & R\cdot + Hg & &
\end{tikzcd}$$

Giese and his coworkers have shown that when such reductions are carried out in the presence of appropriate olefins, the organic radicals may be trapped (52):



Examples were given for cyclohexyl-, n-hexyl- and tert-butylmercuric halides. Olefins which reacted in this manner included $CH_2{=}CHCN$, $CH_2{=}CHCOMe$, $CH_2{=}CHCHO$, $CH_2{=}CHPh$, $CH_2{=}CMeCN$, $CH_2{=}CMeCO_2Me$, $CH_2{=}CCl_2$, and others with electron-withdrawing substituents. The success of this olefin alkylation procedure is very dependent on the reaction conditions, as detailed studies showed. Further studies were devoted to the regioselectivity (53), stereoselectivity (54), temperature effects on selectivity (55) and polar effects (56) in this radical addition process.

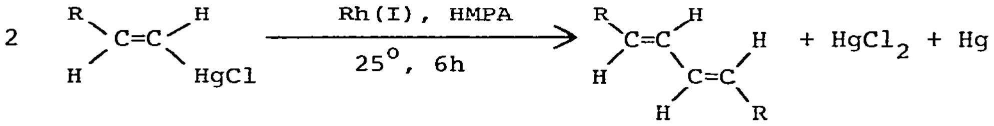
Dialkylmercurials also can induce the radical polymerization of vinyl monomers. The resulting polymers contain RHg end-groups. When such RHg-terminated polymers are treated with a catalytic amount of $SnCl_4 \cdot 5H_2O$ in the presence of another vinyl monomer, block copolymers are produced (57). It was suggested that the RHg termini of the original polymer are activated toward further radical propagation by the $SnCl_4$ as shown below.



$$\sim\!\sim\!CHgR + SnCl_4 \longrightarrow RHgCl + SnCl_3\cdot + \sim\!\sim\!C\cdot$$

3. Transition-Metal Catalyzed Processes

In general, transition metal-catalyzed organomercurial reactions proceed via organotransition metal intermediates which are formed either by substituent transfer from mercury to the transition metal or by oxidative addition of the mercurial to the transition metal center. The rhodium-catalyzed substituent dimerization of vinyl- and of arylmercurials gives symmetrical 1,3-dienes and biaryls, respectively (58):



The most effective catalysts were found to be $RhCl_3 \cdot nH_2O$ and $Cl_2Rh_2(CO)_4/LiCl$. Table 2 presents the examples reported.

The biaryl synthesis required higher reaction temperatures:

$$2\ ArHgCl \xrightarrow[4LiCl,\ HMPA,\ 80^{\circ},\ 24h]{0.5\%\ \ Cl_2Rh_2(CO)_4} Ar\text{-}Ar + HgCl_2 + Hg$$

Results are shown in Table 3. A disadvantage of these reactions is that HMPA is required as solvent, a material which is carcinogenic in rats and causes testicular atrophy. The catalytic cycle shown below was proposed. Such coupling also was found to be catalyzed by $(Ph_3P)_3RhCl$ (59). Here also, HMPA

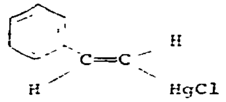
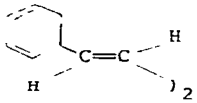
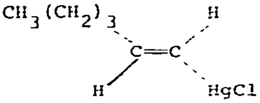
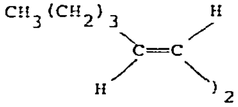
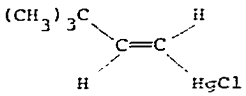
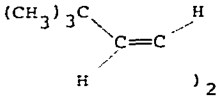
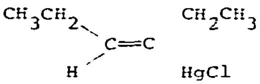
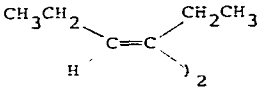
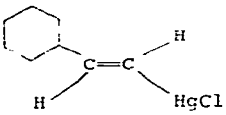
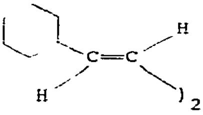
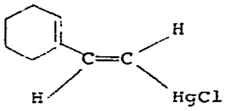
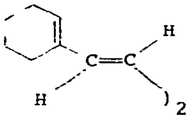
$$RHgCl + RhCl \longrightarrow RhR + HgCl_2$$

$$RhR + RHgCl \longrightarrow R_2RhHgCl$$

$$R_2RhHgCl \longrightarrow R\text{-}R + RhCl + Hg$$

(Continued on p. 161)

Table 2. Synthesis of 1,3-Dienes (58).

Vinylmercurial	Catalyst[a]	Solvent	Diene	Yield,%[b]
	$RhCl_3 \cdot \underline{n}H_2O$	HMPA		65
	$[ClRh(CO)_2]_2$			100
		THF		84
	$RhCl_3 \cdot \underline{n}H_2O$	HMPA		85
	$[ClRh(CO)_2]_2$			100
		THF		99
	$RhCl_3 \cdot \underline{n}H_2O$	HMPA		98
	$[ClPh(CO)_2]_2$			100(88)
		THF		100
	$RhCl_3 \cdot nH_2O$	HMPA		24[c]
	$[ClRh(CO_2)]_2$			35[c]
				(90)
		THF		(97)
		HMPA		(92)

a) 1% "rhodium" and 2 equiv. of lithium chloride per vinylmercurial.

b) GLC analysis (isolated yield). c) Reactions run at 75°C.

Table 3. Synthesis of Biaryls (58).

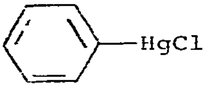
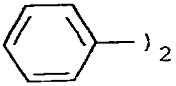
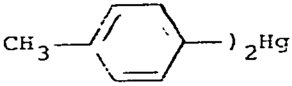
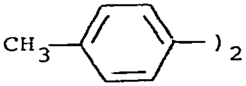
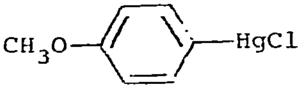
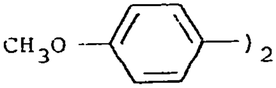
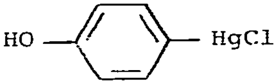
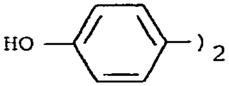
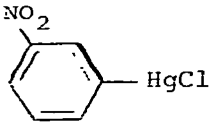
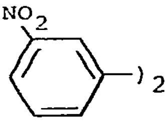
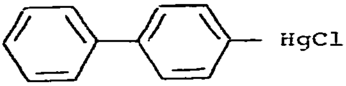
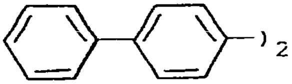
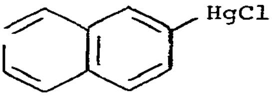
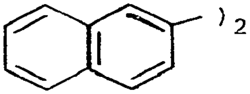
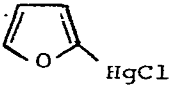
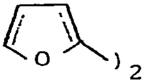
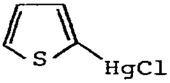
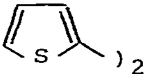
Arylmercuric Chloride	Biaryl	Isolated Yield, %
		84
		92
		88
		88
		53
		40
		94
		70
		96

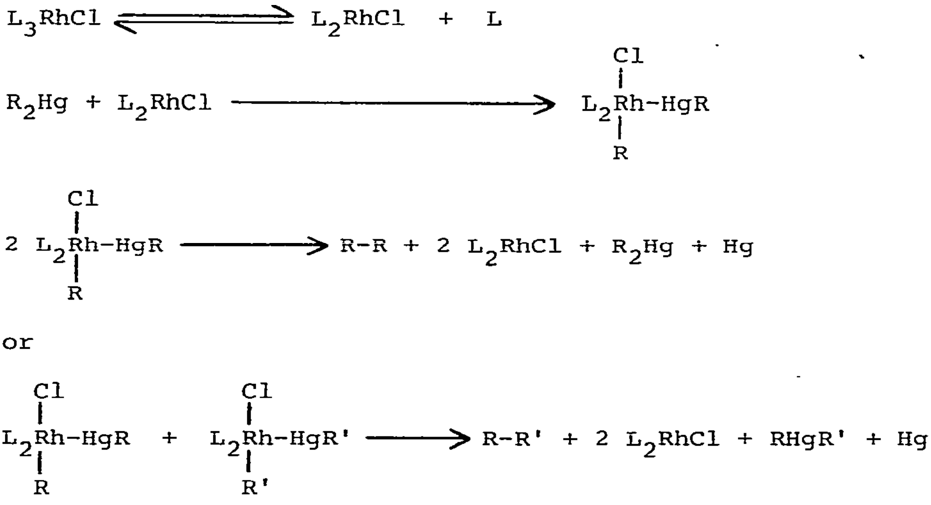
Table 4. $(Ph_3P)_3RhCl$-Catalyzed $R_2Hg \rightarrow R\text{-}R$ Conversions (in HMPA) (59)

R in R_2Hg	Temperature (°C)	Reaction Time (Hr.)	% Yield of Product
Ph	80	4	100
$PhC{\equiv}C$	50	1	95
(E)-PhCH=CH	70	1	99
$p\text{-}MeC_6H_4$	80	4	86
$p\text{-}ClC_6H_4$	80	4	91
$PhCH_2$	130	8	44

proved to be the solvent of choice. Results are collected in Table 4. Di-*n*-butyl-mercury did not react. Such coupling of a mixture of diarylmercurials, Ar_2Hg and Ar'_2Hg, gave a nearly statistical mixture of biaryls:

$$Ph_2Hg + (p\text{-}MeC_6H_4)_2Hg \xrightarrow{Rh(I)} 1\ Ph\text{-}Ph + 2\ Ph\text{-}C_6H_4Me\text{-}p$$
$$+ 1\ p\text{-}MeC_6H_4\text{-}C_6H_4Me\text{-}p$$

This requires a mechanism of the type shown below.



$$L_3RhCl \rightleftharpoons L_2RhCl + L$$

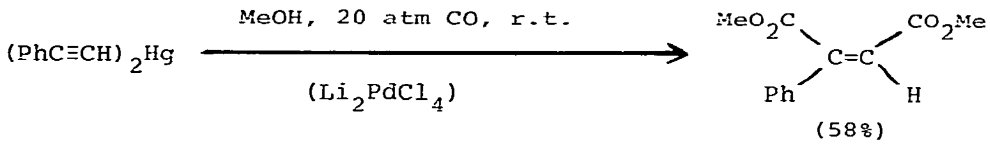
$$R_2Hg + L_2RhCl \longrightarrow L_2\overset{\mathrm{Cl}}{\underset{\mathrm{R}}{\mathrm{Rh}}}\text{-}HgR$$

$$2\ L_2\overset{\mathrm{Cl}}{\underset{\mathrm{R}}{\mathrm{Rh}}}\text{-}HgR \longrightarrow R\text{-}R + 2\ L_2RhCl + R_2Hg + Hg$$

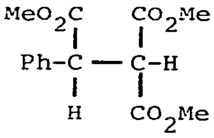
or

$$L_2\overset{\mathrm{Cl}}{\underset{\mathrm{R}}{\mathrm{Rh}}}\text{-}HgR + L_2\overset{\mathrm{Cl}}{\underset{\mathrm{R'}}{\mathrm{Rh}}}\text{-}HgR' \longrightarrow R\text{-}R' + 2\ L_2RhCl + RHgR' + Hg$$

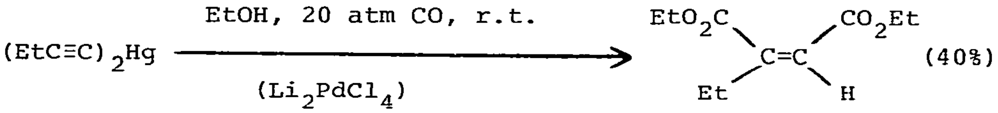
The alkoxycarbonylation of $(RC{\equiv}C)_2Hg$ (R = Ph, Et) is catalyzed by Pd(II) salts (60):



Minor by-products were methyl phenylpropiolate (4%) and dimethyl phenylfumarate (4%). When this reaction was carried out at 100°C, there was an additional product:

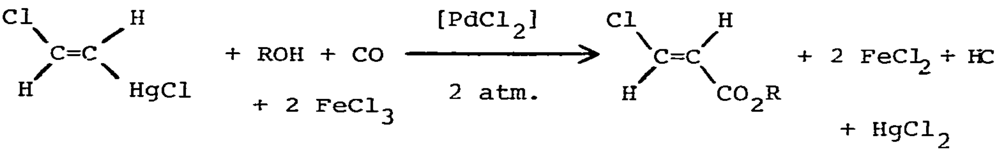


$(EtC{\equiv}C)_2Hg$ reacted similarly:



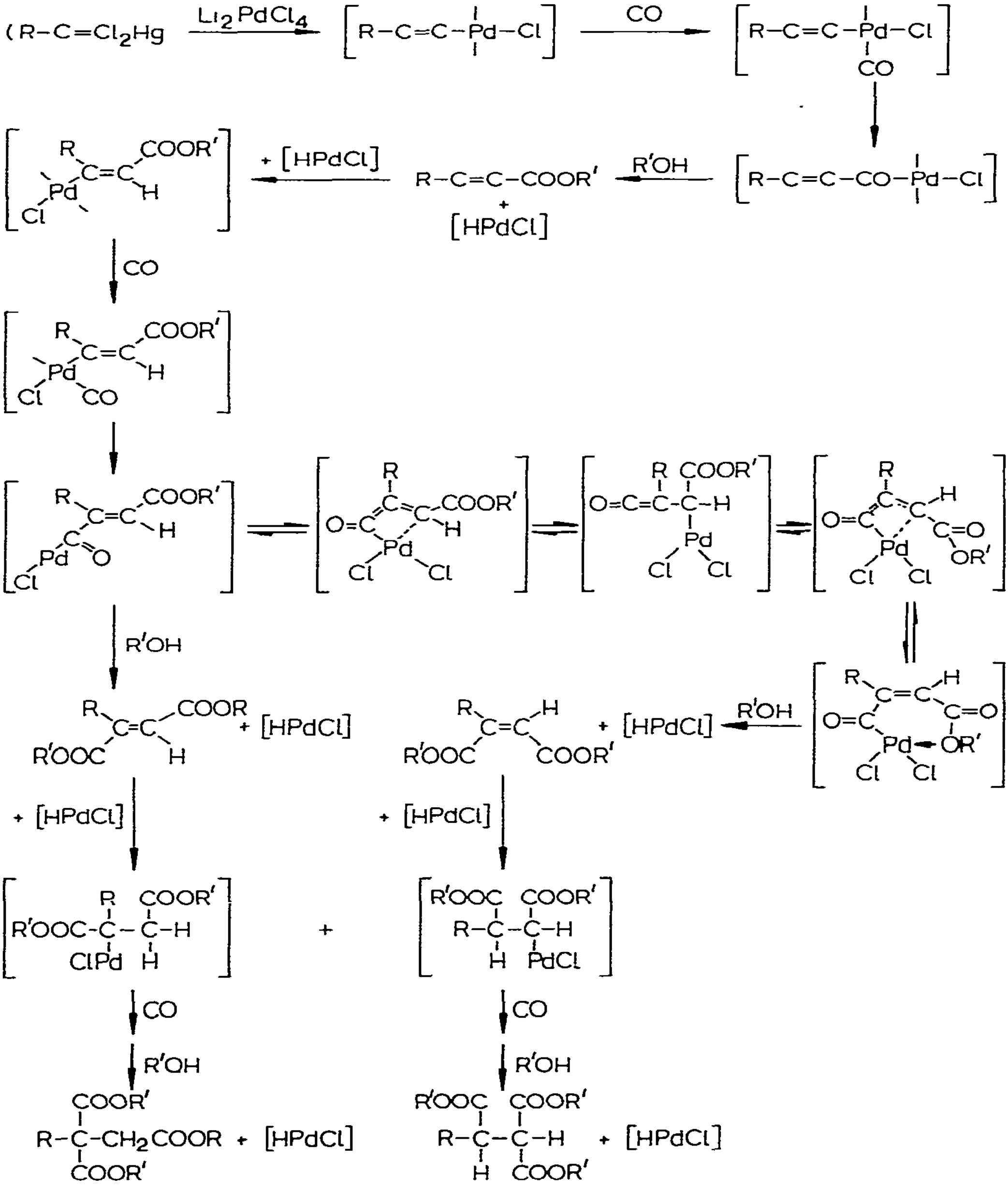
(+ diethyl ethylfumarate (10%) and ethyl 2-pentynoate (16%))

The reaction course shown in Scheme 1 was proposed. Palladium(II) chloride also catalyzes the alkoxycarbonylation of trans-β-chlorovinylmercuric chloride (61):



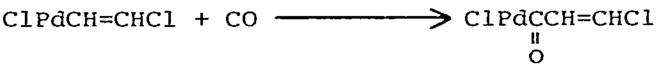
(ROH = an alcohol or water)

Scheme 1

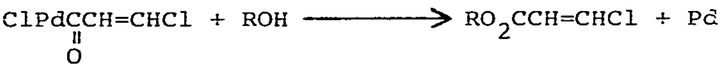

(R-C≡C)₂Hg
Li₂PdCl₄
CO
R'OH
+ [HPdCl]
R-C≡C-COOR'
+ [HPdCl]
CO
R'OH
+ [HPdCl]
CO
R'OH
+ [HPdCl]
+ [HPdCl]
CO
R'OH
+ [HPdCl]

The kinetics of this process were studied. The following mechanism was suggested:

$$ClCH{=}CHHgCl + PdCl_2 \longrightarrow ClPdCH{=}CHCl + HgCl_2$$



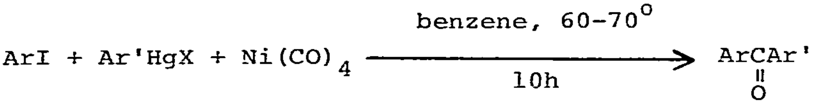
$$ClPdCH{=}CHCl + CO \longrightarrow ClPd\overset{O}{\overset{\|}{C}}CH{=}CHCl$$



$$ClPd\overset{O}{\overset{\|}{C}}CH{=}CHCl + ROH \longrightarrow RO_2CCH{=}CHCl + Pd$$

$$Pd + 2\ FeCl_3 \longrightarrow PdCl_2 + 2\ FeCl_2$$

Unsymmetrical ketones can be prepared by reaction of an aryl iodide with an arylmercuric halide in the presence of nickel tetracarbonyl (62):

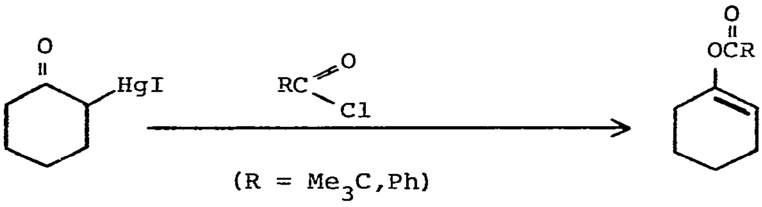


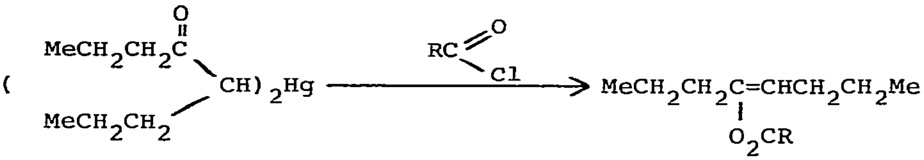
$$ArI + Ar'HgX + Ni(CO)_4 \xrightarrow[10h]{benzene,\ 60\text{-}70^o} Ar\overset{O}{\overset{\|}{C}}Ar'$$

Product yields were good, but this synthesis has the disadvantage that it requires use of the highly toxic nickel tetracarbonyl as a stoichiometric reagent.

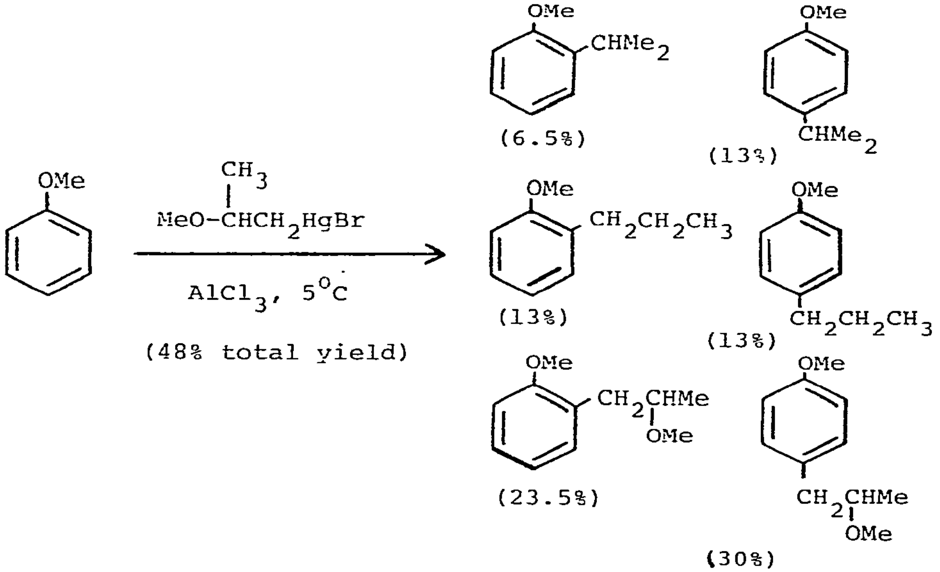
4. Miscellaneous

The reaction of α-ketomercurials with acyl chlorides gives enol esters (63):

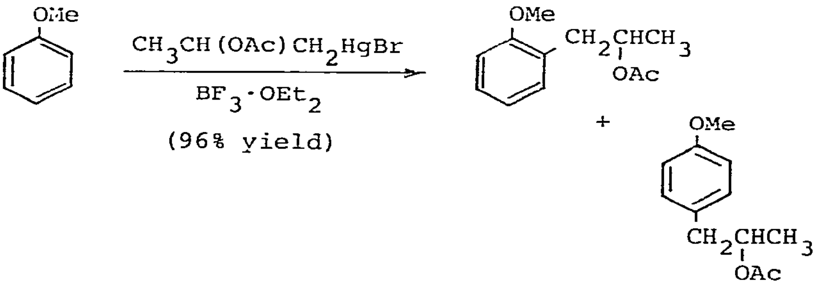




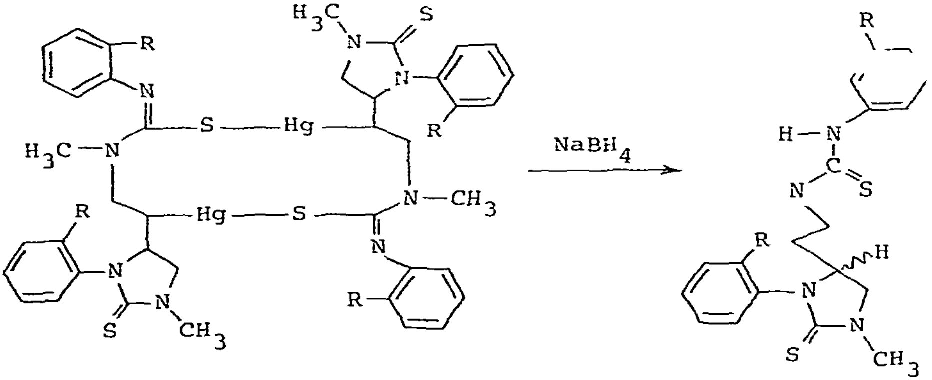
β-Oxy-functional ethylmercuric halides react with aromatic compounds in the presence of Lewis acids. A mixture of products generally results (64).



Similar reactions were carried out with $CH_3CH(OH)CH_2HgBr$ and $CH_3CH(OAc)CH_2HgBr$. Best results, in terms of introducing functional substituents into the aromatic ring, were obtained using boron trifluoride diethyl etherate as catalyst:



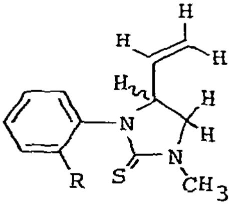
The reduction of substituted 2,8-dithia-4,10-diaza-1,7-dimercuracyclododecanes is of preparative utility (65):



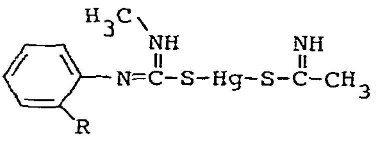
(R = H, Me)

7

Thioacetamide reacted with 7 to give 8 and decomposition products of 9.

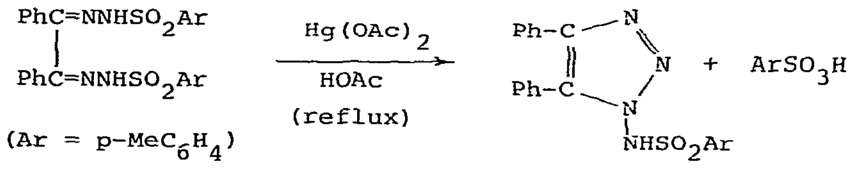


8



9

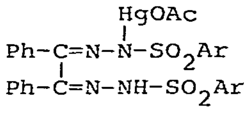
The oxidation of benzilbis(toluene-p-sulfonyl)hydrazone with mercuric acetate resulted in formation of 10 (66). When



(Ar = p-MeC$_6$H$_4$)

10

this reaction was carried out in cold acetic acid, the unstable organomercury intermediate involved in this process, 11, could be isolated. This decomposed to give 10.



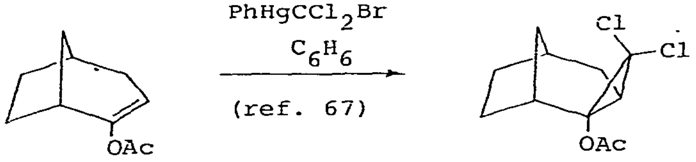
$$\begin{array}{l}\qquad\qquad\ \ \text{HgOAc}\\ \qquad\qquad\quad\ |\\ \text{Ph-C=N-N-SO}_2\text{Ar}\\ \qquad |\\ \text{Ph-C=N-NH-SO}_2\text{Ar}\end{array}$$

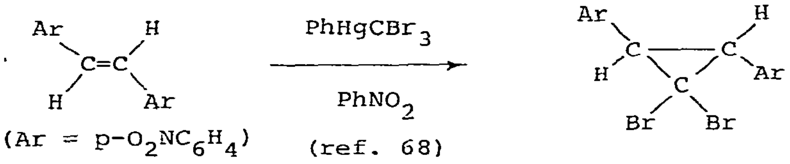
11

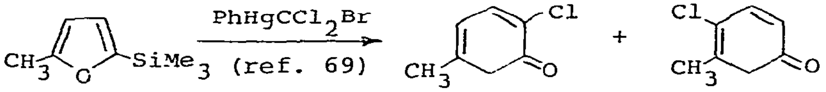
C. Halomethyl-Mercury Compounds

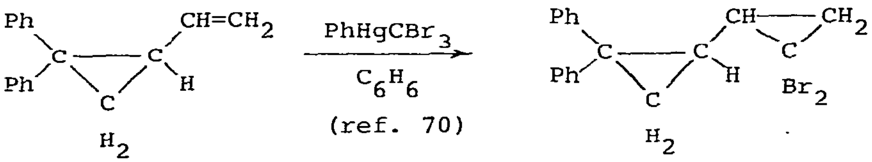
A review which covers the chemistry of this class of compounds, with emphasis on questions of mechanism, has been published (4).

New divalent carbon transfer reactions of phenyl(trihalomethyl)-mercury compounds with olefins have been reported:

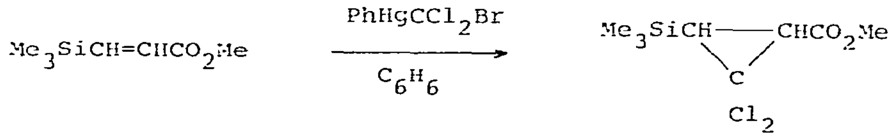




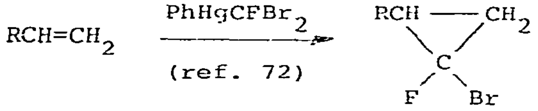




(2 isomers)

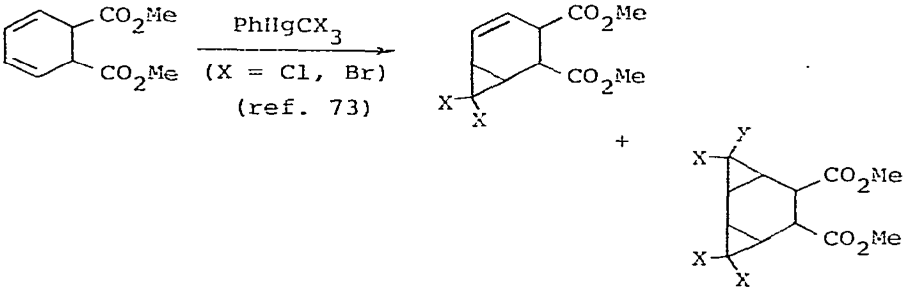


Reactions were carried out with the pure cis and trans isomers and, as expected, were found to be stereospecific (71).



(mixture of syn and anti isomers)

(R = mesityl, C_6F_5, PhO, C_6H_5)



These examples generally represent the "tough" cases where conventional dihalocarbene generating systems don't work well or not at all.

Further examples of insertion reactions of $PhHgCX_3$-derived dihalocarbenes have been reported by Weidenbruch and his coworkers. Into silicon hydrides:

$$(Me_3C)_3SiH + PhHgCCl_3 \xrightarrow[\text{(ref. 74)}]{120^\circ} (Me_3C)_3SiCHCl_2 \quad (53\%)$$

$$(Me_3C)_3SiH + PhHgCBr_3 \xrightarrow[\text{(ref. 74)}]{120^\circ} (Me_3C)_3SiCHBr_2 \quad (54\%)$$

Into Group IV halides (75):

$$Cl_3Si\text{-}SiCl_3 + PhHgCCl_2X \xrightarrow{NaI,\ 120^o} Cl_3CSiCl_2SiCl_3$$
$$(X = Cl,\ Br)$$

$$GeCl_4 + PhHgCCl_2Br \xrightarrow{NaI,\ 100^o} Cl_3GeCCl_3$$

In contrast:

$$\begin{tikzcd}
SnCl_4 + PhHgCCl_2Br \arrow[r] & PhSnCl_3 + ClHgCCl_2Br \arrow[d, "CCl_2"] \\
 & CCl_3HgCCl_2Br \arrow[d] \\
 & CCl_3HgBr + CCl_2
\end{tikzcd}$$

(isolated Hg product)

$$Br_3Si\text{-}SiBr_3 + PhHgCCl_3 \xrightarrow{NaI,\ 105^o} Br_3SiSiBr_2CCl_2Br$$

$$SiBr_4 + PhHgCCl_3 \xrightarrow{NaI,\ 120^o} Br_3SiCCl_2Br$$

$$GeBr_4 + PhHgCCl_3 \xrightarrow{NaI,\ 90^o} Br_3GeCCl_2Br$$

Similar CCl_2 insertion into Group IV tetraiodides was not successful.

The reaction of $PhHgCCl_3$ with bromoform at 80° gave a 3:1:8 mixture of $HCCl_3$, $HCCl_2Br$ and $HCClBr_2$. Presumably, a sequence of steps of the type shown below was responsible for the formation of these products (76):

$$PhHgCCl_3 \longrightarrow PhHgCl + CCl_2$$
$$CCl_2 + HCBr_3 \longrightarrow CBr_2 + HCCl_2Br$$
$$CBr_2 + PhHgCl \longrightarrow PhHgCClBr_2$$

Bis(α-chlorovinyl)mercury also underwent what appears to be α-elimination when treated with Cu(I)/triisopropyl phosphite combinations (8):

$$\mathrm{Hg(CCl{=}CH_2)_2 + 2\ (RO)_3P\cdot CuI \xrightarrow{r.t.} 2\ HC{\equiv}CH\cdot CuI + (RO)_3P\cdot HgCl_2 + (RO)_3P}$$

and,

$$\mathrm{Hg(CCl{=}CH_2)_2 + (RO)_3P_2CuH \longrightarrow HC{\equiv}CH + Hg + (RO)_3P\cdot CuCl + (RO)_3P + CH_2{=}CHCl}$$

The acetylene presumably was formed by rearrangement of a $CH_2{=}C{:}$ intermediate. The bis(α-chlorovinyl)mercury was prepared by the organolithium route. Bis(β-chlorovinyl)mercury showed similar elimination chemistry:

$$\mathrm{Hg(CH{=}CHCl)_2 + (RO)_3P\cdot CuI \longrightarrow 2\ HC{\equiv}CH\cdot CuI + (RO)_3P\cdot HgCl_2 + (RO)_3P}$$

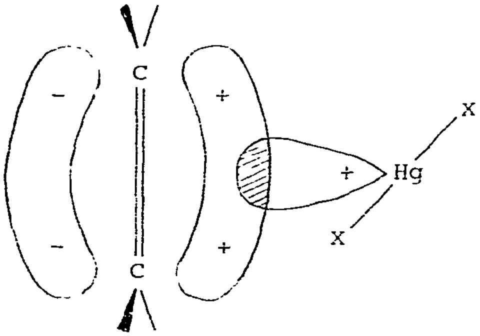
Here, of course, it is β-elimination which takes place.

4. MERCURATION OF UNSATURATED COMPOUNDS

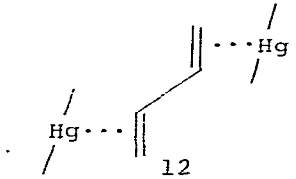
The most important organomercury application in organic syntheses involves the (solvo)mercuration of olefins, dienes, acetylenes, cyclopropanes and aromatic compounds followed by reactions which replace the mercury substituent by hydrogen, halogen or other functions. In many instances, the organomercurial is formed *in situ* and is never isolated at all. Its presence and its structure in those cases are inferred from the structure of the organic product.

A. Olefins

Full details have been provided of the matrix isolation/IR spectroscopy studies by Nakamoto and his coworkers on mercury halide/olefin systems (HgX_2, with X = F, Cl, Br, I; olefin = C_2H_4, C_3H_6, 1,3-butadiene) (77). 1:1 Complexes were prepared by cocondensation of mercuric halide vapor with the olefin diluted with argon on a ca. 10°K cesium iodide IR window. Evidence also was obtained for a $2HgCl \cdot 1CH_2{=}CH{-}CH{=}CH_2$ complex. The IR spectroscopic results were discussed in terms of a side-on structure in which the olefin plane is parallel and its C=C axis perpendicular to the X-Hg-X axis, with appreciable overlap of the ethylene 2p pi MO and the vacant metal orbital:

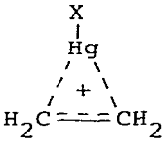


The 1:1 $HgCl_2$/1,3-butadiene complex was suggested to involve side-on coordination of $HgCl_2$ to one of the C=C bonds of the diene. The 2:1 complex was depicted as 12. Such interaction may well play a role in the olefin solvomercuration reaction.



12

Structural effects on reactivity in the oxymercuration reaction have been studied by a Canadian group (78). The transition state of the oxymercuration of olefins which do not contain strongly resonance electron-donating substituents (e.g. ethylene) was indicated to be bridged and with very little positive charge on carbon, 13. On the other hand, olefins with strongly reson-



13

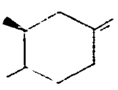
ance electron-donating substituents (e.g. cyclopropyl) reacted via a transition state which resembles an open carbonium ion. Some relative and absolute rates of olefin methoxymercuration are given in Tabl. 4a and 5. The solvation of the transition state in the oxymercuration of cinnamic acid in alcohol medium has been investigated by Balyatinskaya (79). Available data were used to calculate transsolvation coefficients of HgX^+ intermediates and of the activated complex.

Our coverage of the solvomercuration of olefins is not meant to be exhaustive. Now that the solvomercuration/demercuration sequence has become a routine organic operation, there are many examples of its application tucked away in the organic literature. We mention some which caught our attention during the past year.

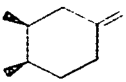
Table 4a. Relative rates of methoxymercuration of alkenes by $Hg(OAc)_2$ in MeOH at 25°C (78)

Alkene	k_{rel}
Cyclohexene	1.0
Norbornene	4.6
1-Octene	7.4
c-$PrCH=CH_2$	700
c-$PrCMe=CH_2$	350
c-$PrCPh=CH_2$	15
c-$Pr_2C=CH_2$	700
cis-4-Octene	0.22
cis-3-Hexene	0.58
tert-$BuCH=CH_2$	0.067
tert-$BuCMe=CH_2$	0.50
tert-$Bu_2C=CH_2$	<0.005

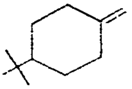
The oxymercuration/demercuration of various methylenecyclohexanes, 14 - 23, was investigated by French workers (80), with



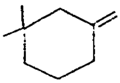
14



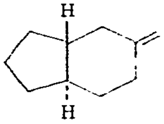
15



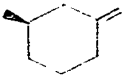
16



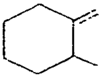
17



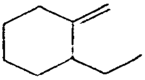
18



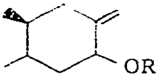
19



20

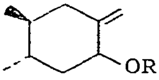


21



(R = H, Me, COMe)

22



(R = H, COMe)

23

particular emphasis on stereochemistry. Methoxymercuration of 4,6-O-benzylidene-D-allal, 24, gave 25 and 26. Demercuration of these products with sodium borohydride produced the anomeric methyl 4,6-O-benzylidene-2-deoxy-D-*ribo*-hexopyranosides 27 and 28, together with various elimination products (81). Also reported have been the oxymercuration/demercuration of *epi*-γ-eudesmol, 29, which gave 30 and 31, presumably *via* 32 and 33 (82), and of 17-methylene-5α-androstan-3β-yl acetate (83). Russian workers have described further studies on the cycliza-

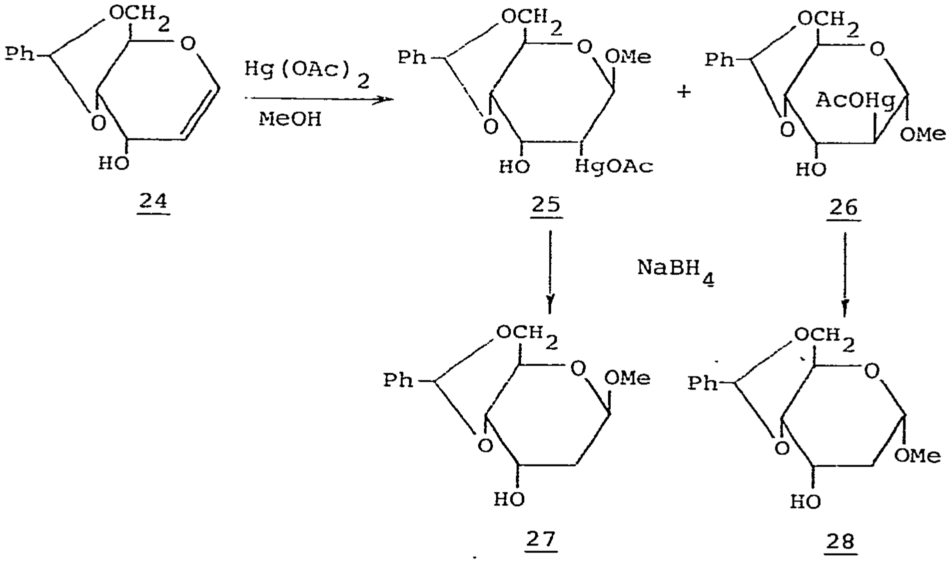
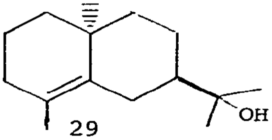


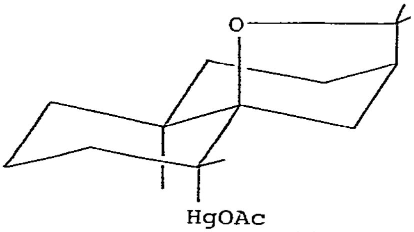
Table 5. Direct measurement of rates of methoxymercuration of alkenes by uv spectroscopy in MeOH at 25°C (78)

Alkene	Methoxymercuration	
	$k_2 (M^{-1}s^{-1})$	k_{rel}
$CH_2=CH_2$	1.04	0.50
n-BuCH=CH_2	2.06	1.0
tert-BuCH=CH_2	0.058	0.028
tert-BuCMe=CH_2	0.50	0.24
c-PrCH=CH_2	840	410
c-PrCMe=CH_2	4300	2100
c-$Pr_2C=CH_2$	5500	2700
c-PrCH=CHMe(Z)	1.37	0.67
c-PrCH=CHMe(E)	0.64	0.31
Cyclohexene	0.50	0.24
Norbornene	5.3	2.6

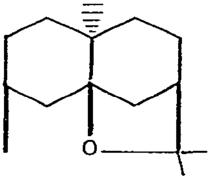
tion of geranylacetone, 34, by mercuric trifluoroacetate,



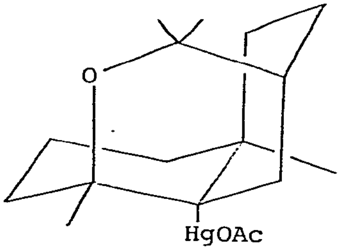
29



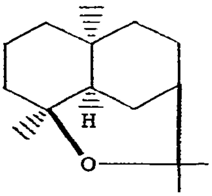
32



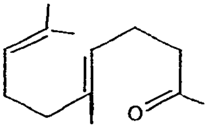
30



33



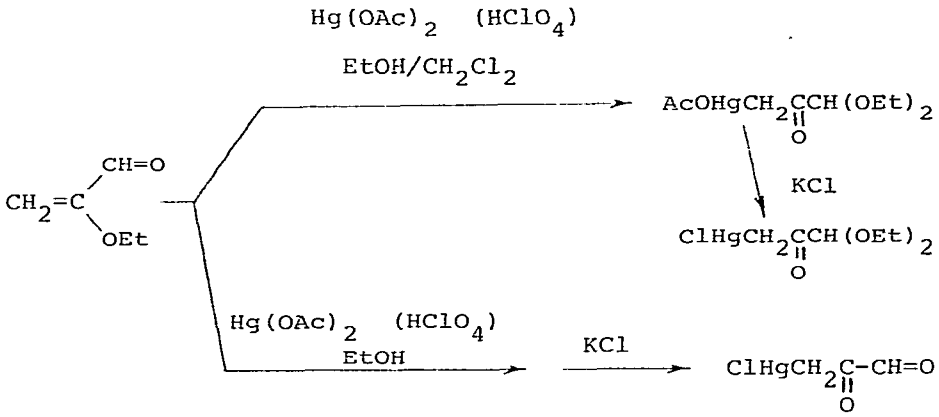
31



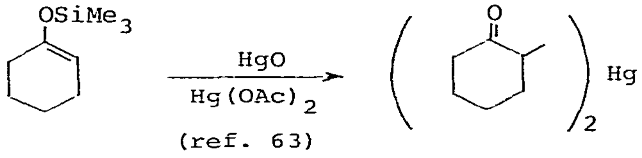
34

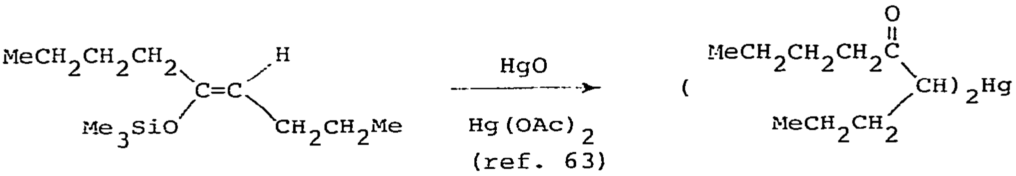
followed by reduction of the mercurial formed with sodium borohydride (84).

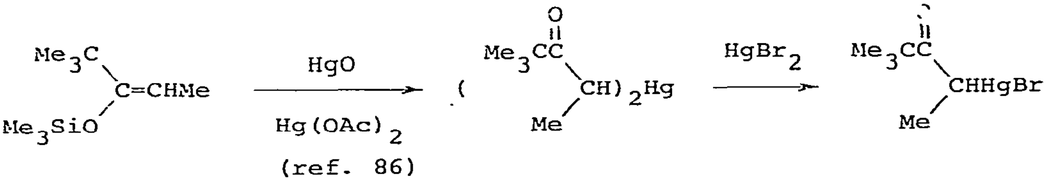
The ethoxymercuration of 2-ethoxyacrolein gave carbonyl-functional mercurials (85):



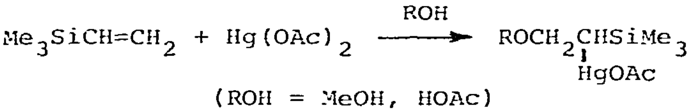
Some examples of the mercuration of enoxysilanes have been reported:





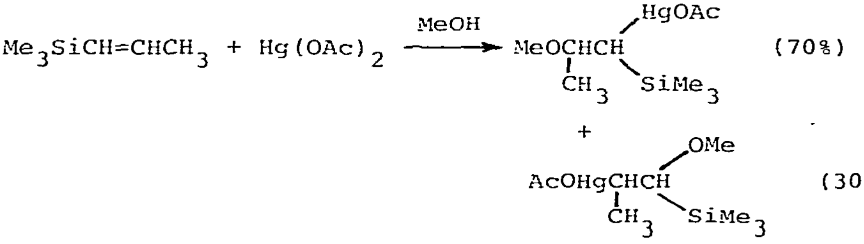


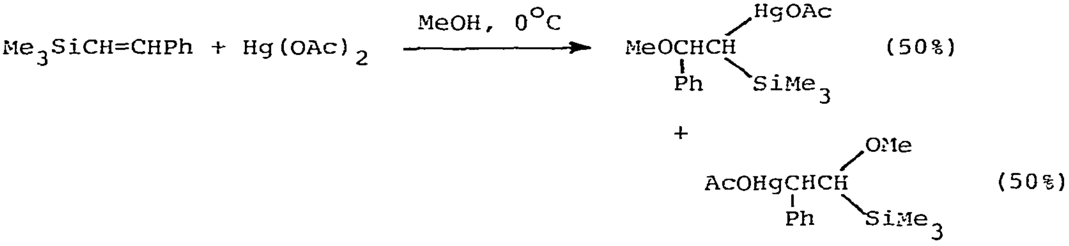
Oxymercuration of alkenylsilanes has been studied (87).



$$Me_3SiCH=CH_2 + Hg(OAc)_2 \xrightarrow{ROH} ROCH_2\underset{HgOAc}{\underset{|}{C}}HSiMe_3$$

(ROH = MeOH, HOAc)

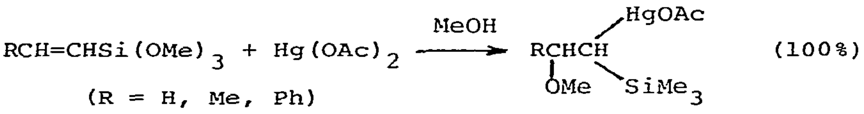




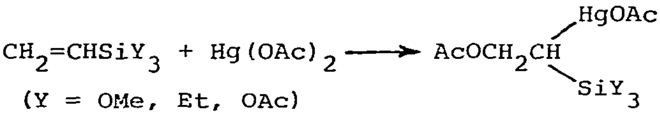
(At 20°, cleavage to give Me_3SiOAc and PhCH=CHHgOAc occurs).

$$Me_3SiCH_2CH=CH_2 + Hg(OAc)_2 \longrightarrow Me_3SiOAc + CH_2=CHCH_2HgOAc$$

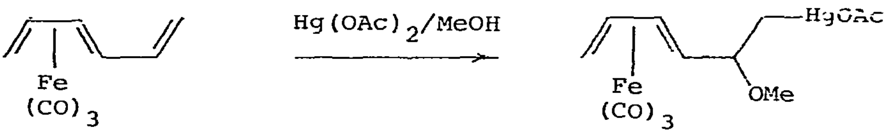
Methoxy substituents on silicon have a strong directive effect:



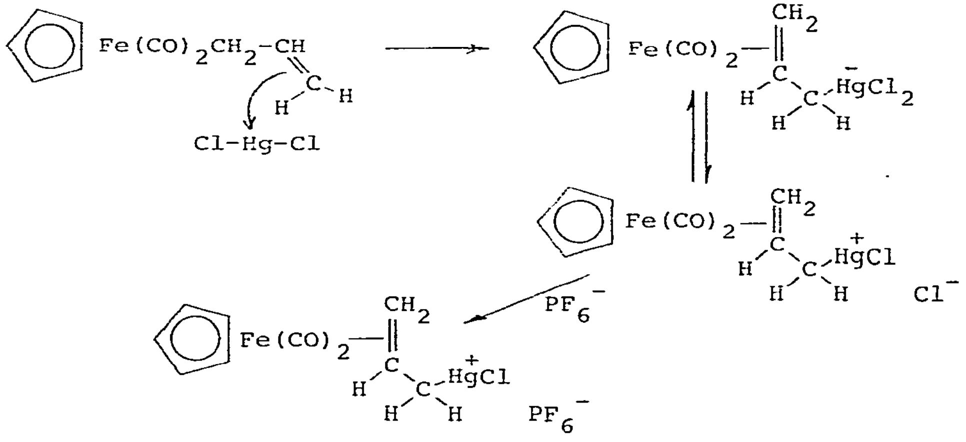
Acetoxymercuration took place in nitromethane or chloroform medium:



Of interest is the methoxymercuration of a coordinated triene (88):

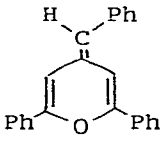


σ-Allyliron complexes reacted with mercuric chloride as shown, the mercuration process being accompanied by a σ to π rearrangement (89):

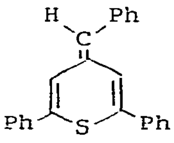


Similar chemistry occurred with $CpFe(CO)_2CH_2CMe{=}CH_2$, but $CpFe(CO)_2$-CH_2R compounds where R = $CH{=}CMe_2$, CH=CHPh and C≡CPh underwent slow Fe-C cleavage on treatment with mercuric chloride. Both types of reaction were observed with $CpFe(CO)_2CH_2CH{=}CHCH_3$.

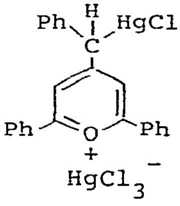
Mercuration of 35 and 36 with mercuric chloride in diethyl ether at reflux gave pyrylium and thiopyrylium salts 37 and 38, respectively (90).



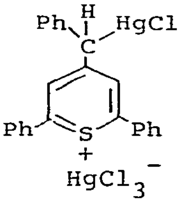
35



36

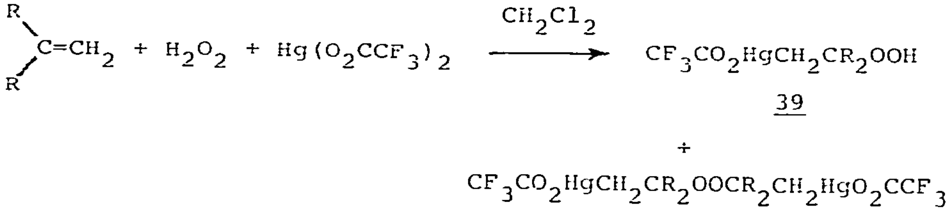


37



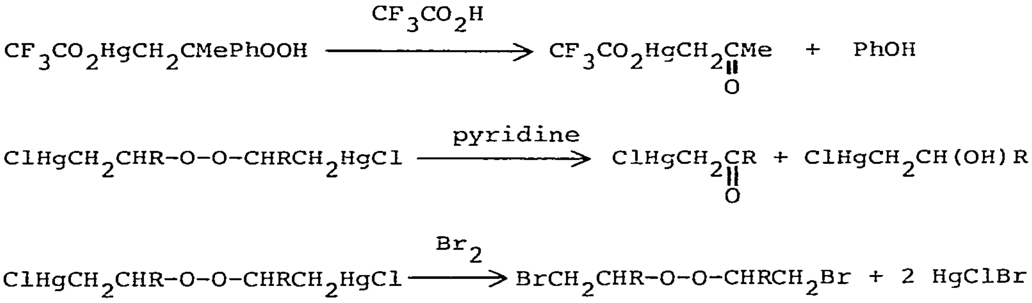
38

Mercuration of terminal olefins with mercuric trifluoroacetate in the presence of 78 - 87% hydrogen peroxide in dichloromethane gave a mixture of β-mercurialkyl hydroperoxide and bis-β-mercurialkyl peroxide (91):



$$R_2C{=}CH_2 + H_2O_2 + Hg(O_2CCF_3)_2 \xrightarrow{CH_2Cl_2} \underset{\underline{39}}{CF_3CO_2HgCH_2CR_2OOH} + CF_3CO_2HgCH_2CR_2OOCR_2CH_2HgO_2CCF_3$$

The hydroperoxide 39 could participate in further peroxymercurations, and in this manner, the mixed species $CF_3CO_2HgCH_2CMe_2$-$OOCHPhCH_2HgO_2CCF_3$ was prepared. The mercurated peroxides which were characterized are shown in Table 6. A brief study of their chemistry was made. Selected reactions are shown below.



$$CF_3CO_2HgCH_2CMePhOOH \xrightarrow{CF_3CO_2H} CF_3CO_2HgCH_2\underset{\underset{O}{\|}}{C}Me + PhOH$$

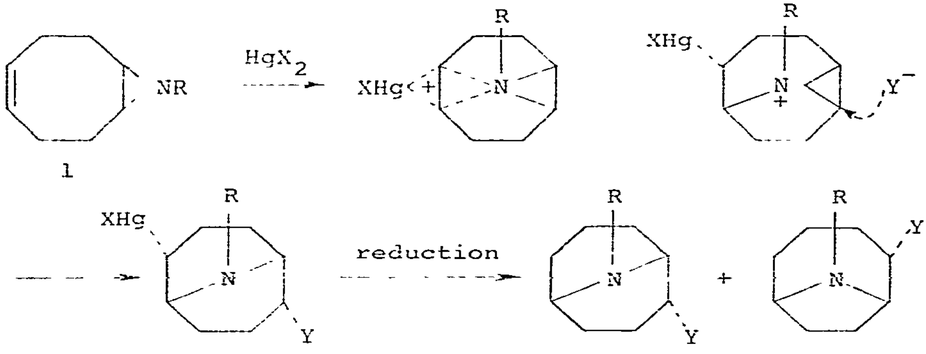
$$ClHgCH_2CHR\text{-}O\text{-}O\text{-}CHRCH_2HgCl \xrightarrow{\text{pyridine}} ClHgCH_2\underset{\underset{O}{\|}}{C}R + ClHgCH_2CH(OH)R$$

$$ClHgCH_2CHR\text{-}O\text{-}O\text{-}CHRCH_2HgCl \xrightarrow{Br_2} BrCH_2CHR\text{-}O\text{-}O\text{-}CHRCH_2Br + 2\ HgClBr$$

Table 6. β-Mercurialkyl hydroperoxides and bis-β-mercurialkyl peroxides ($XHg{\cdot}CH_2{\cdot}CR^1R^2{\cdot}O{\cdot}OR$)

Parent alkene(s)	X	R^1	R^2	R	M.p. (°C)
Phenylethene	OAc	Ph	H	H	115-116
2-Methylpropene	$CF_3{\cdot}CO_2$	Me	Me	H	83
2-Phenylpropene	$CF_3{\cdot}CO_2$	Ph	Me	H	90-91
Ethene	Cl	H	H	$CH_2{\cdot}CH_2{\cdot}HgCl$	149-150
Propene	$CF_3{\cdot}CO_2$	Me	H	$CHMe{\cdot}CH_2{\cdot}Hg{\cdot}O_2C{\cdot}CF_3$	109-110.5
Phenylethene	Cl	Ph	H	$CHPh{\cdot}CH_2{\cdot}HgCl$	148-150
2-Methylpropene	$CF_3{\cdot}CO_2$	Me	Me	$CMe_2{\cdot}CH_2{\cdot}Hg{\cdot}O_2C{\cdot}CF_3$	122.5-124
2-Methylpropene and phenylethene	$CF_3{\cdot}CO_2$	Me	Me	$CHPh\ CH_2{\cdot}Hg{\cdot}O_2C{\cdot}CF_3$	96-97

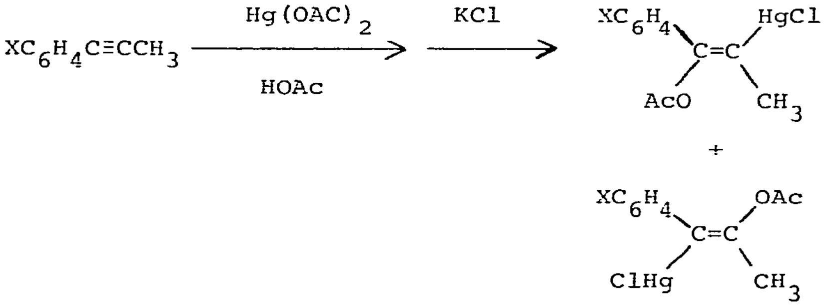
Intramolecular aminomercuration of unsaturated cyclic aziridines has been reported by French workers (92). The general scheme shown below was followed.



(Y⁻ = X⁻ or solvent)

B. Acetylenes

The acetoxymercuration of substituted 1-aryl-1-propynes has been investigated (93):



40

41

In general, both isomers were formed (Table 7). Trans stereochemistry was observed, without exception. Noteworthy is the preference for AcO⁻ attack at the benzylic position, a tendency which decreases as substituents are introduced which decrease the ability of the aromatic ring to stabilize an adjacent positive charge. A mercurinium mechanism was favored:

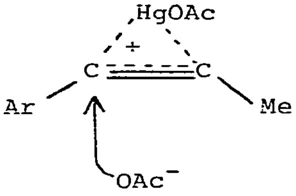
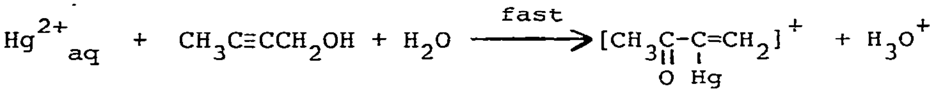


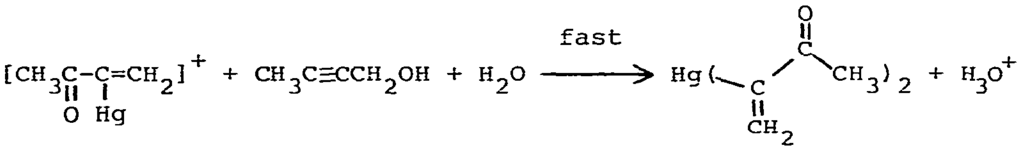
Table 7. Yields and Isomer Ratios: Acetoxymercuration of Substituted 1-Aryl-1-propynes (93).

X in $XC_6H_4C\equiv CCH_3$	40/41 Ratio	Crude Yield (40 + 41)
p-OMe	only 40	93
p-Me	14.0/1	89
p-F	8.7/1	85
H	2.85/1	84
p-Cl	2.9/1	80
p-Br	1.95/1	83
m-Cl	1.1/1	50

A study of the kinetics and mechanism of the Hg(II)-catalyzed hydration/isomerization of 2-butyn-1-ol has been carried out. An organomercury mechanism was found to obtain (94):

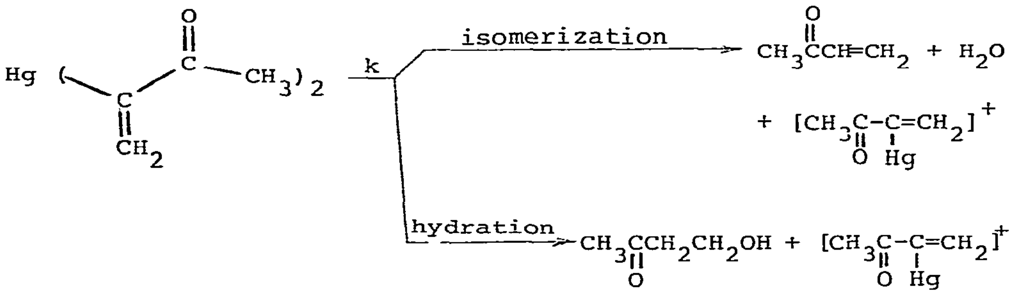


$$Hg^{2+}_{aq} + CH_3C\equiv CCH_2OH + H_2O \xrightarrow{fast} [CH_3\underset{O}{\underset{\|}{C}}-\underset{Hg}{\underset{|}{C}}=CH_2]^+ + H_3O^+$$

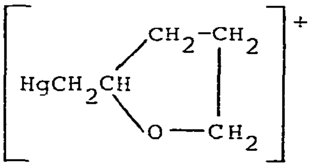


$$[CH_3\underset{O}{\underset{\|}{C}}-\underset{Hg}{\underset{|}{C}}=CH_2]^+ + CH_3C\equiv CCH_2OH + H_2O \xrightarrow{fast} Hg(C(=CH_2)C(=O)CH_3)_2 + H_3O^+$$

42



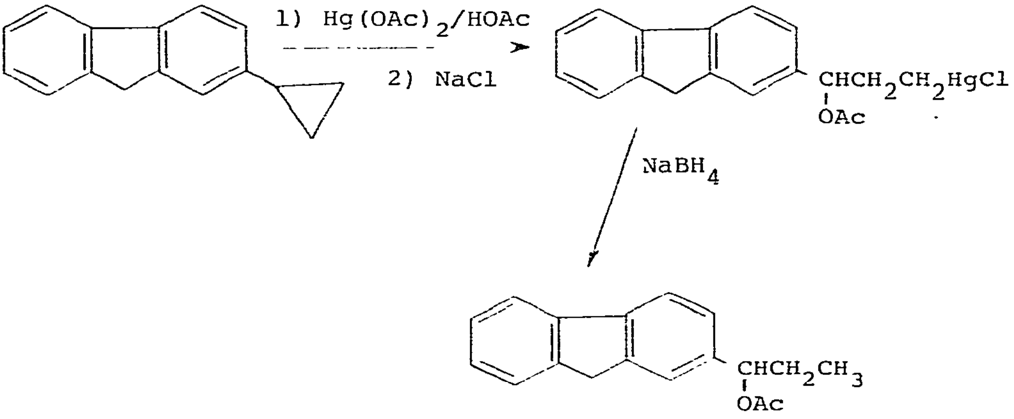
Mercurial 42 was isolated and characterized in a separate experiment. Catalysis also was effected with 43, which was prepared by adding 4-penten-1-ol to the reaction solution.



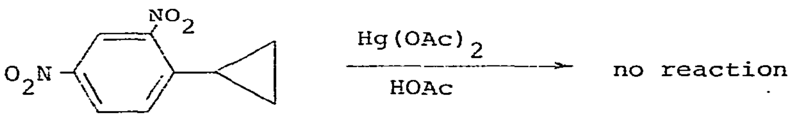
43

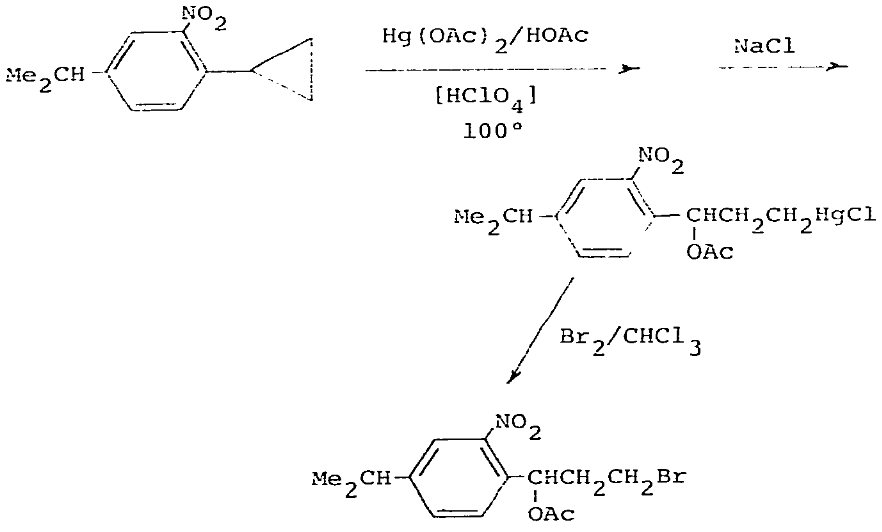
C. Cyclopropanes

Shabarov and his coworkers have continued their studies of cyclopropane mercuration. In the acetoxymercuration of the isomeric 1-cyclohexyl-2-phenylcyclopropanes complete inversion of configuration did not occur at the site of acetate ion attack (95). The cyclopropyl group of 2-cyclopropylfluorene is more readily opened by mercuric acetate than are those of arylcyclopropanes (Ar = H, p-Ph, p-Me_3C) (96):

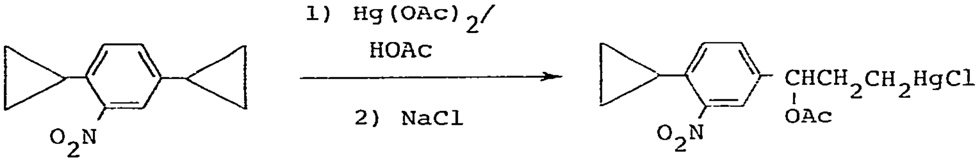


A nitro group on an aromatic ring deactivates a cyclopropane ring toward reaction with mercuric acetate (97):





In methanol the methyl ether was produced rather than the acetoxy derivative. These reactions required more strenuous conditions (perchloric acid catalyst, elevated temperatures) than are usually needed for the solvomercuration of arylcyclopropanes. Also reported was:

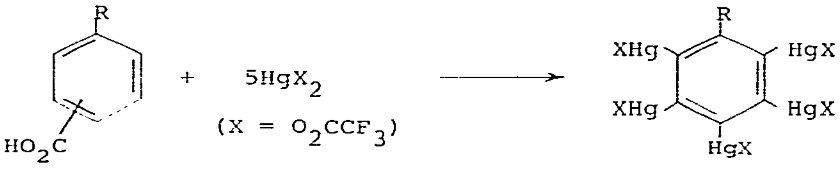


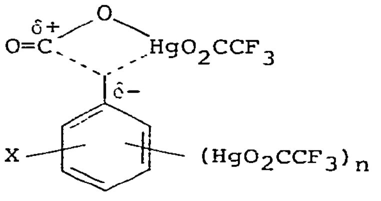
Here also a reaction temperature of 100° was required. When the reaction was carried out in methanol, a reaction temperature of 65° sufficed.

D. Aromatic Compounds

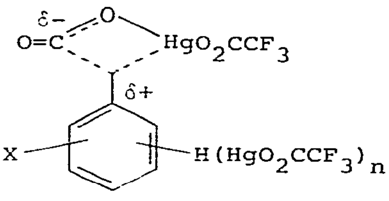
Deacon and Farquharson have continued their studies of the permercuration of arenes and of the further reactions of the permercurated products (50); cf. Table 1 in Section 3-B.

It is noteworthy that benzoic acid and substituted benzoic acids were at least partially, often totally, decarboxylated under the rather strenuous reaction conditions (180-245°C), while p-toluenesulfonic acid lost sulfur trioxide. The results of a detailed study of this aspect are given in Table 8 (49). The ease of decarboxylation during permercuration increases in the order $p\text{-}XC_6H_4CO_2H \leq m\text{-}XC_6H_4CO_2H < o\text{-}XC_6H_4CO_2H$, regardless of the nature of X. A four-center S_E2 transition state with some polar character, 44 and 45, was suggested. Here transition state 44 is facilitated by inductive effects of electron-withdrawing substituents and 45 by inductive effects of electron-releasing substituents.





44



45

The permercuration of ferrocene has been reported by Russian workers (98):

$$\begin{tikzcd}{[C_5H_5]_2Fe} \arrow[r, "Hg(O_2CCF_3)_2"] & {Fe[C_5(HgO_2CCF_3)_5]_2} \arrow[dr, "KCl"] & \\ & & {Fe[C_5(HgCl)_5]_2}\end{tikzcd}$$

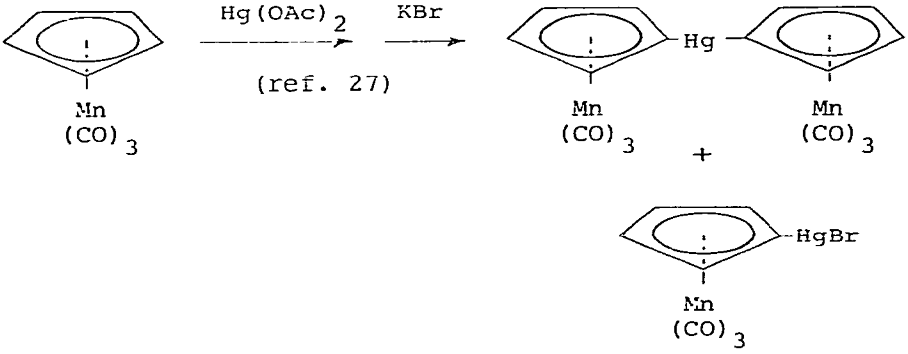
$$Fe[C_5(HgO_2CCF_3)_5]_2 + 5\ I_3^- \xrightarrow{H_2O} Fe[C_5I_5]_2$$

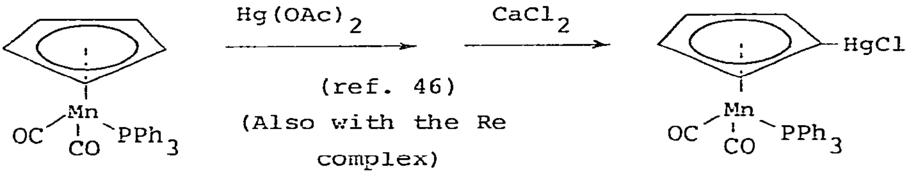
Table 8. Permercuration and bromodemercuration of monosubstituted benzoic acids (49). (Amounts of 10 mmol of acid and 70 mmol of mercuric trifluoroacetate were used.)

X in $XC_6H_4CO_2H$	Permercuration* temperature (°C)	Yield(%) of $XC_6Br_4CO_2H$	Yield(%) of C_6Br_5X
o-Me	180	25	58
m-Me	180	57	28
p-Me	200	c.0·5	84
m-F	210	20	45
p-F	210	57	29
o-Cl	200	3	80
m-Cl	200	63	26
p-Cl	200	58	27
o-Br	200	12	65
m-Br	200	52	25
p-Br	200	52	30
o-MeO	180	--	73
m-MeO	200	19	53
p-MeO	180	--	70
o-NO_2	240	--	55
m-NO_2	240*	11	61
p-NO_2	240	37	43
o-CF_3	245	--	56
m-CF_3	245	2	76
p-CF_3	245	6	74
H	180	65	22 } C_6Br_6
H	215	38	50

*Reaction times c. 3 min. for o-MeO and p-MeO, c. 20 min. for reactions at 240-245°, and 5-10 min. for others.

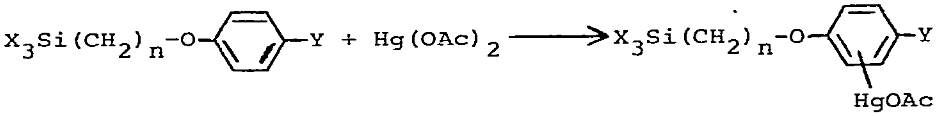
The much greater reactivity of ferrocene in the permercuration reaction is striking. Mercuration of other η^5-cyclopentadienyl complexes has been described:





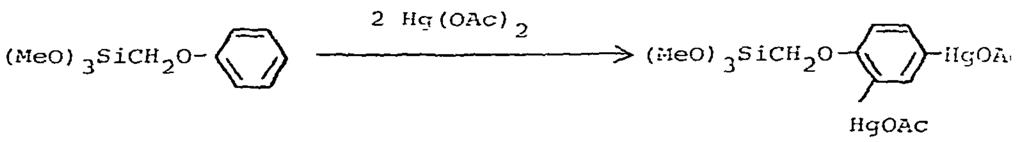
Pentafluorobenzene is readily mercurated to give $(C_6F_5)_2Hg$ in good yield by Hg_2F_2, HgO and $Hg(O_2CCF_3)_2$ in antimony pentafluoride solution (5).

Alkyl phenyl ethers containing organosilicon substituents in the alkyl group have been mercurated (99):

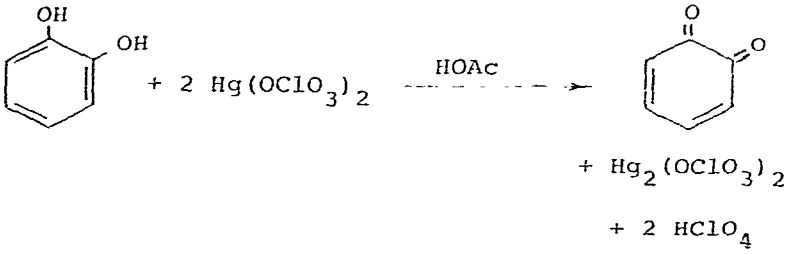


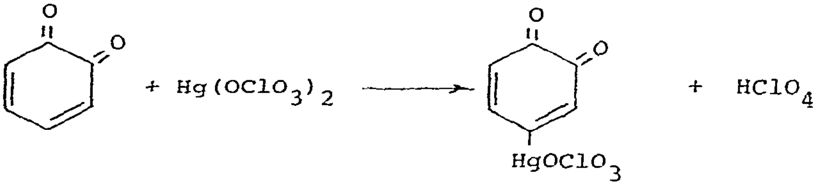
X	n	Y
Me	1	o-OMe
Et	1	H
MeO	1	H
MeO	3	H
EtO	1	p-Me

(When Y = H, the mercuration product was the para isomer.)

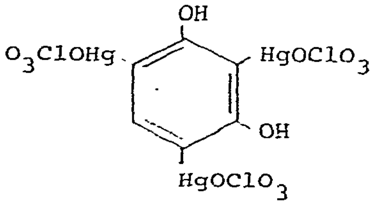


Kinetic data suggested that the action of mercuric ion on pyrocatechol in acetic acid results in oxidation and subsequent mercuration (100):



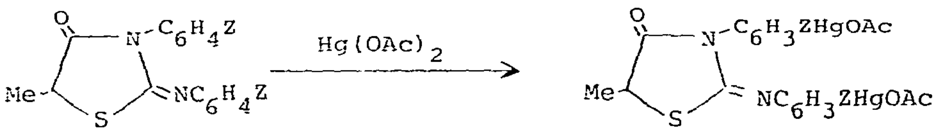


Resorcinol was trimercurated to give 46.



46

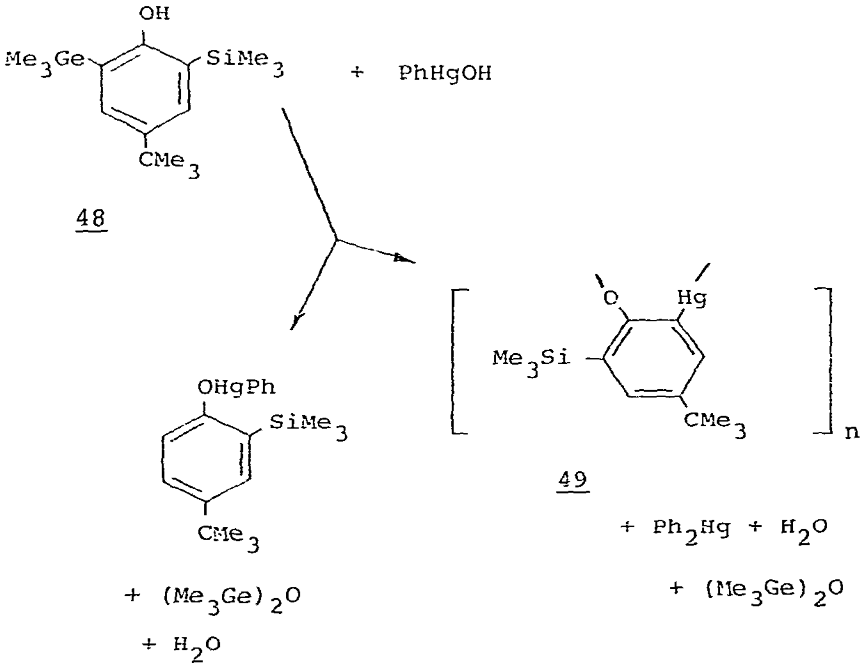
The kinetics of the redox mercuration of fifteen other benzenediols were studied. Also reported has been the mercuration of aryl(arylimino)thiazolidones, 47, (101) and of the o, m and p isomers of the $HOC_6H_4CO_2Co^{III}(NH_3)_5^{2+}$ cation (102).



47

Z = m-F, p-F, m-NO_2, p-NO_2,
m-OH, p-OH, o-OH, p-OH.

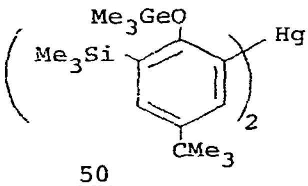
The reaction of phenylmercuric hydroxide with phenol 48 resulted in part in a mercurated product (103):



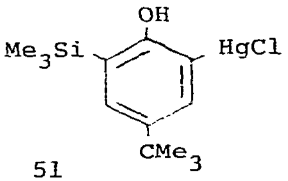
48

49

Polymer 49 is the hydrolysis product of the initially formed product, 50. The polymer reacts with HCl to give 51.

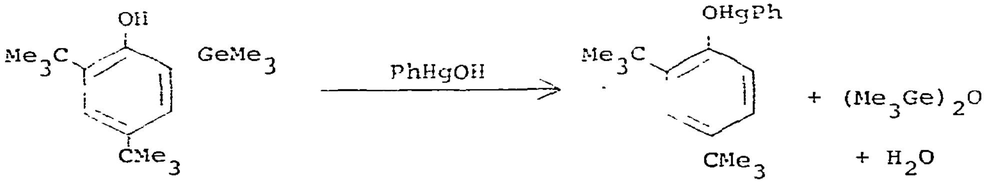


50

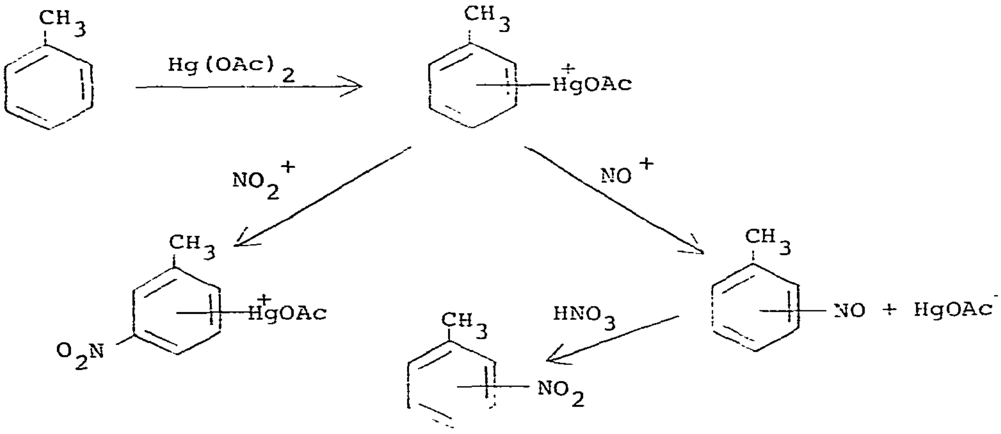


51

Also reported was:

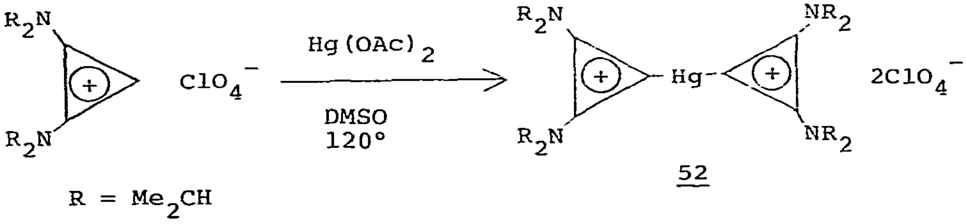


Finally, arene mercuration products are intermediates in mercuric salt-catalyzed nitration of toluene (104):

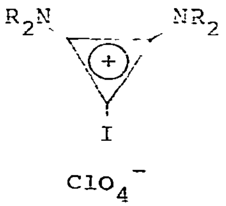


5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS

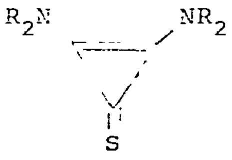
The reaction of diaminocyclopropenium perchlorate with mercuric acetate gave a cationic diaminocyclopropenylidene complex (105):



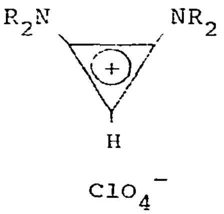
The large $J(^{13}C-^{199}Hg)$ coupling constant (2508 Hz) observed in the ^{13}C NMR spectrum of this product served to show that sp hybridization of mercury was involved. Some reactions of 52 were carried out: reactions with iodine, with sulfur and with acid gave 53, 54 and 55, respectively.



53



54



55

Sulfur-functional mercurials were studied by Chivers and Ram (9). It was found that $Hg[CH(SPh)_2]_2$ undergoes C-Hg bond homolysis on thermal decomposition:

$$Hg[CH(SPh)_2]_2 \xrightarrow{\text{slow}} (PhS)_2CH\cdot \; + \; (PhS)_2CHHg\cdot$$

$$(PhS)_2CHHg\cdot \xrightarrow{\text{fast}} (PhS)_2CH\cdot \; + \; Hg(0)$$

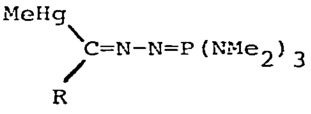
The final products of decomposition at 150°C in vacuo were $(PhS)_3CH$, $(PhS)_2CH_2$, $(PhS)_2CHCH(SPh)_2$ and elemental mercury. Similar thermolysis of $PhHgCH(SPh)_2$ at 120°C gave elemental mercury, diphenylmercury, $(PhS)_3CH$ and $(PhS)_2CH_2$. No evidence for a carbene pathway, i.e., $PhHgCH(SPh)_2 \longrightarrow PhHgSPh + HCSPh$, was found.

The reaction of dimethylsulfoxonium methylide, $Me_2\overset{+}{S}(O)-CH_2^-$, with methylmercuric chloride gave a product which was assigned the structure $[Me_2S(O)CH_2HgMe]Cl$ (106). Reactions of this ylide with 1,2 and 3 molar equivalents of mercuric chloride resulted in formation of adducts, $[Me_2S(O)CH_2]_n\cdot HgCl_2$, with $n = 1$, 2 and 3. The structures of these could not be determined. Already mentioned in Section 2-F is the novel mercury/phosphorus ylide complex 6 (35), which was isolated in the form of pale yellow, air-sensitive crystals. The low $^{199}Hg-C-^{1}H$ coupling constant observed in the proton NMR spectrum of 6 was in line with the assumed sp^3 hybridization of its mercury atom.

Further results on the chemistry of mercurated diazoalkanes have been reported by Lorberth. A new, explosive mercurated diazoalkane was prepared (107):

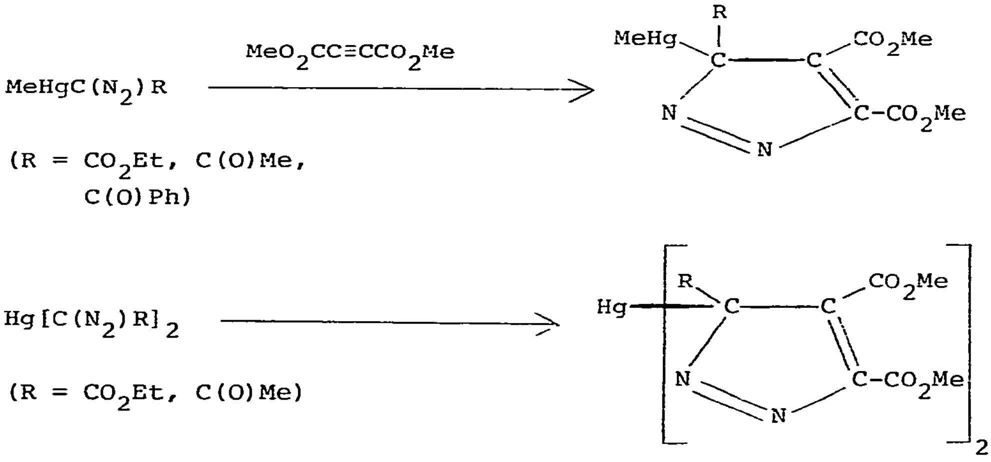
$$2\ Hg[N(SiMe_3)_2]_2 + Me_2AsCHN_2 \longrightarrow Hg[C(N_2)AsMe_2]_2$$

$MeHgC(N_2)CO_2Et$, $MeHgC(N_2)C(O)CH_3$ and $MeHgC(N_2)C(O)Ph$ formed 1: complexes (phosphazines) with $P(NMe_2)_3$ of type 56. $Hg[C(N_2)CO_2Et]_2$ forms 1:1 and 1:2 complexes, $(Me_2N)_3P{=}N{-}N{=}C(CO_2Et)HgC(N_2)CO_2Et$ and $[(Me_2N)_3P{=}N{-}N{=}C(CO_2Et)]_2Hg$ with this

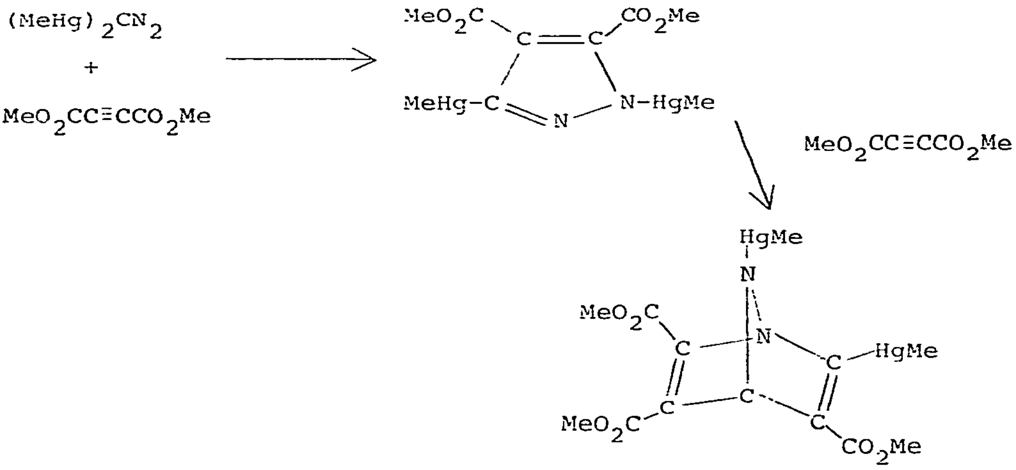


56

phosphine (108). All of these phosphazines were isolated in the form of yellow crystals. Mercurated diazoalkanes undergo 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate (109):

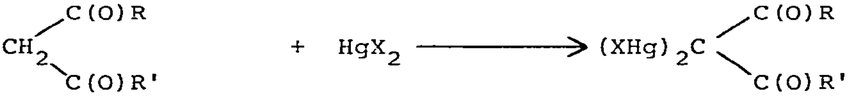


On the other hand, the reaction of $(MeHg)_2CN_2$ with two molar equivalents of dimethyl acetylenedicarboxylate gave the diazonorbornadiene 57:



57

^{13}C NMR spectroscopy has been used to establish the C-Hg bonded structures of $Me_3CC(O)CHMeHgBr$ and $(Me_3CC(O)CHMe)_2Hg$ (86). Reactions of mercuric oxide with diethyl malonate, ethyl acetoacetate and ethyl cyanoacetate (but not with malononitrile) gave Hg-C bonded products, $Hg[CH(CO_2Et)R]_2$ ($R = CO_2Et$, C(O)Me, CN, respectively) (110). Also reported were the following preparations:



$$CH_2\begin{matrix}C(O)R\\C(O)R'\end{matrix} + HgX_2 \longrightarrow (XHg)_2C\begin{matrix}C(O)R\\C(O)R'\end{matrix}$$

R,R' = OEt, OEt
OEt, Me
Me, Me

X = Cl, Br,
OAc

$$RCH_2CN + HgX_2 \longrightarrow (XHg)_2C\begin{matrix}R\\CN\end{matrix}$$

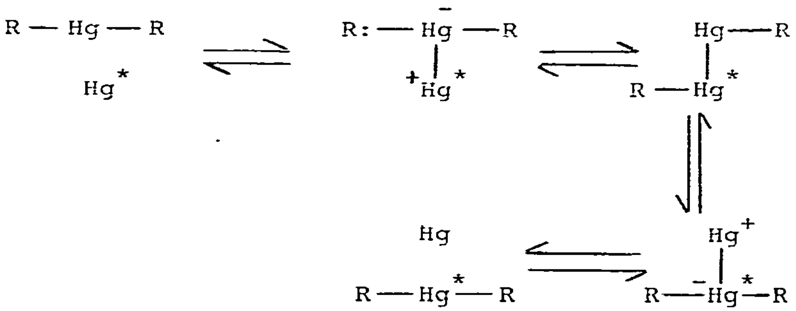
($R = EtO_2C$, CN; X = Cl, OAc)

Detailed studies of the IR, NMR and mass spectra of these products were reported.

6. MERCURY-CARBON BOND REACTIONS

Those C-Hg bond reactions which have demonstrated synthet utility have been discussed in Section 3.

A discussion of the R_2Hg/Hg mercury exchange reaction has been presented in terms of qualitative molecular orbital considerations (111). The authors contend that these confirm the mechanism which they proposed previously on the basis of kinetic, stereochemical and electrochemical studies:



Reutov and his coworkers have described further studies of the substituent exchange reactions between organomercurials:

$$R_2Hg + HgYZ \rightleftharpoons RHgY + RHgZ$$

(Y, Z = organic or inorganic substituent).

Equilibrium constants have been determined by a polarographic method for the $R_2Hg/Hg(CN)_2$ (Table 9) and various $R_2Hg/R'HgY$ systems (Table 10) in DMF solution (112). In the latter system the equilibrium is displaced to the right, i.e., to RHgX + RHgR', in those cases where the electronegativity of R is lower than that of R'. An approach which considers both the complexing properties of the organomercury(II) cations and the stability of the carbanions of the exchanging groups, R^- and R'^-, served to explain these results. Solvent effects on the disproportionation reaction:

$$2\ C_6F_5HgC_6H_5 \overset{K}{\rightleftharpoons} (C_6F_5)_2Hg + (C_6H_5)_2Hg$$

have been investigated by the polarographic method (113). At 20°C, in the presence of 0.1M R_4N^+ salt, the following equilibrium constants ($K \times 10^3$) were determined: in DMF containing

Table 9. The Equilibrium of Exchange Reactions $Hg(CN)_2 + HgR_2 \rightleftharpoons 2RHgCN$ in DMF in the Presence of 0.1 M Bu_4NClO_4 (initial concentrations of organomercury compounds 1×10^{-2} M) (112).

Reaction No.	R in R_2Hg	Temp.	K_e
1	$Ph_2C{=}CH$	25°	>100
2	CH_3OCOCH_2	100	8.3
		40	3.8
3	C_6F_5	100	3.6
4	$PhC{\equiv}C$	100	1.1

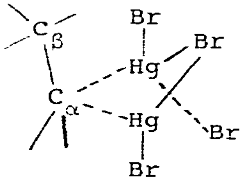
Table 10. The Equilibrium of the Exchange Reactions between Organomercury Compounds and Organomercury Salts in DMF in the Presence of 0.1 M Bu_4NClO_4 at 25°C (112).

Reaction No.	Reaction	K_e
1	$Ph_2Hg + CH_3OCOCH_2HgBr \rightleftharpoons PhHgCH_2COOCH_3 + PhHgBr$	1.7
2	$Ph_2Hg + CH_3COCH_2HgBr \rightleftharpoons PhHgCH_2COCH_3 + PhHgBr$	2.2
3	$Ph_2Hg + C_6F_5HgBr \rightleftharpoons PhHgC_6F_5 + PhHgBr$	24
4	$(C_6F_5)_2Hg + C_2H_5HgBr \rightleftharpoons C_6F_5HgC_2H_5 + C_6F_5HgBr$	$\ll 1$
5	$C_6F_5HgPh + PhHgBr \rightleftharpoons C_6F_5HgBr + Ph_2Hg$	$\ll 1$
6	$C_6F_5HgPh + PhHgOCOCF_3 \rightleftharpoons C_6F_5HgOCOCF_3 + Ph_2Hg$	$\ll 1$
7	$C_6F_5HgC_2H_5 + C_6H_5HgCl \rightleftharpoons C_6F_5HgCl + (C_2H_5)_2Hg$	$\ll 1$
8	$C_6F_5HgPh + C_2H_5HgCl$ – $\rightleftharpoons C_6F_5HgCl + C_2H_5HgPh$ (a)	$\ll 1$
	$\rightleftharpoons C_6F_5HgC_2H_5 + PhHgCl$ (b)	Polarographic method unsuitable
9	$C_6F_5HgC_2H_5 + PhHgX$ – (X=Br, I, CF_3COO) $\rightleftharpoons C_6F_5HgPh + C_2H_5HgX$ (a)	
	$\rightleftharpoons C_6F_5HgX + PhHgC_2H_5$ (b)	$\ll 1$
10	$C_6F_5HgPh + C_6F_5HgC_2H_5 \rightleftharpoons (C_6F_5)_2Hg + PhHgC_2H_5$	0.07

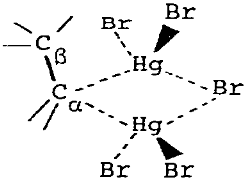
added I^-, 19±2; in DMSO, 11±1; in sulfolane, 4.6±0.5; in CH_3CN, 4.6±0.5; in DMF, 4.3±0.5. The effect of iodide ion on the rates of such exchange reactions was investigated as well (114). Added iodide ion accelerated exchange in the $Ph_2Hg/(PhC{\equiv}C)_2Hg$ system, retarded it in exchange reactions of Ph_2Hg with $Hg(CN)_2$, HgI_2 and $HgBr_2$ and had practically no effect in the $Ph_2Hg/$

$Hg(CCl_3)_2$ system. Possible explanations of these results were discussed.

Calculations have been carried out to assess the steric effect of a neopentyl group (compared with that of a methyl group) in the $RHgBr/HgBr_2$ substituent exchange reaction in ethanol (115). Both the one-Br^- and two-Br^- catalyzed reactions were considered. The calculations using the symmetrical, bicyclic model with two bridging bromide ions, 58, (Jensen and Rickborn, 1958) provided good agreement with experiment in the case of the one-anion catalysis. The observed $Me_3CCH_2HgBr/MeHgBr$ rate ratios in the case of the two-anion catalyzed process agreed well with that calculated for a symmetrical, cyclic transition state, 59.



58



59

The cleavage of cyclopentadienylmercuric bromide in aqueous solution containing bromide ion by perchloric acid has been the subject of a kinetic study (116). A mechanism involving fast, reversible complexing of Br^- to the mercury atom (giving $RHgBr_2^-$, $RHgBr_3^{2-}$ and even $RHgBr_4^{3-}$) followed by rate-determining acidolysis of the C-Hg bond in these complexes was indicated. (A study of the substituent exchange reactions, i.e., exchange reactions with HgX_2, RHgX and R_2Hg, of cyclopentadienylmercury could be of considerable interest in view of the high reactivity of these compounds, due in large part to the pronounced carbanionic nature of the cyclopentadienyl substituent.)

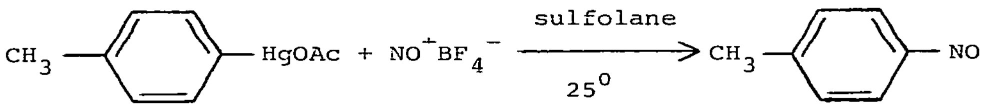
${}^{14}C$-Scrambling in the products of the cleavage of $CH_3CH_2CH_2$-${}^{14}CH_2HgClO_4$ by trifluoroacetic acid showed that at 35°C the only scrambling processes were those involving successive 1,2-hydride shifts in classical 1- and 2-butyl cations (117):

$$\begin{tikzcd} CH_3CH_2CH_2{}^{14}CH_2HgClO_4 \arrow[r, "H^+"] & CH_3CH_2CH_2{}^{14}CH_2Hg^+ \arrow[d, "- Hg"] \\ & CH_3CH_2CH_2{}^{14}CH_2^+ \end{tikzcd}$$

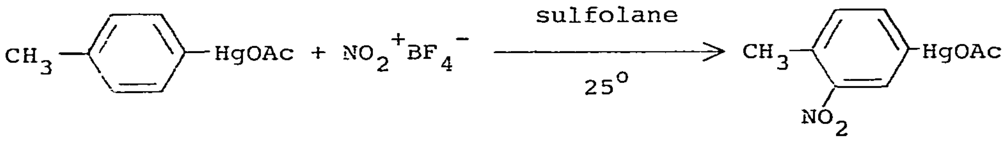
$$CH_3CH_2CH_2{}^{14}CH_2^+ \rightleftharpoons CH_3CH_2\overset{+}{C}H{}^{14}CH_3 \rightleftharpoons CH_3\overset{+}{C}HCH_2{}^{14}CH_3$$

At higher temperatures (50° or 72°C), however, equilibrating protonated methylcyclopropanes appeared to become involved.

The reactions of p-tolylmercuric acetate with NO^+ and NO_2^+ salts have been examined by Stock and Wright during the course of their study of the Hg(II)-catalyzed nitration of toluene (104).



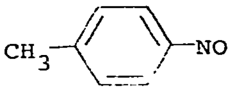
(96%)



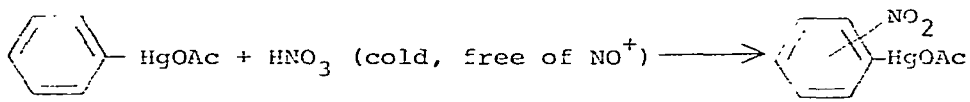
(major product)

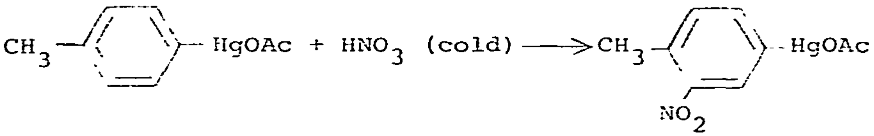
+ lesser amounts of

and



but:





It appears that NO^+ undergoes the nitrosodemercuration reaction with arylmercuric acetates, but, on the other hand, NO_2^+ undergoes nitrodeprotonation rather than nitrodemercuration.

The complicated chemistry which occurs in R_2Hg/CCl_4 systems has been investigated in great detail by Nugent and Kochi (118, 119, 120). These reactions can be initiated photochemically or with radical species obtained by peroxide thermolysis. Evidence was presented for a free radical chain process which involves β-hydrogen abstraction from R_2Hg by trichloromethyl radicals, followed by elimination and fragmentation of alkylmercury radicals and by subsequent chain transfer with carbon tetrachloride:

$$CCl_4 \longrightarrow Cl_3C\cdot$$

$$H\text{-}CMe_2CH_2HgR + Cl_3C\cdot \longrightarrow \cdot CMe_2CH_2HgR + HCCl_3$$

$$\cdot CMe_2CH_2HgR \longrightarrow Me_2C{=}CH_2 + RHg\cdot$$

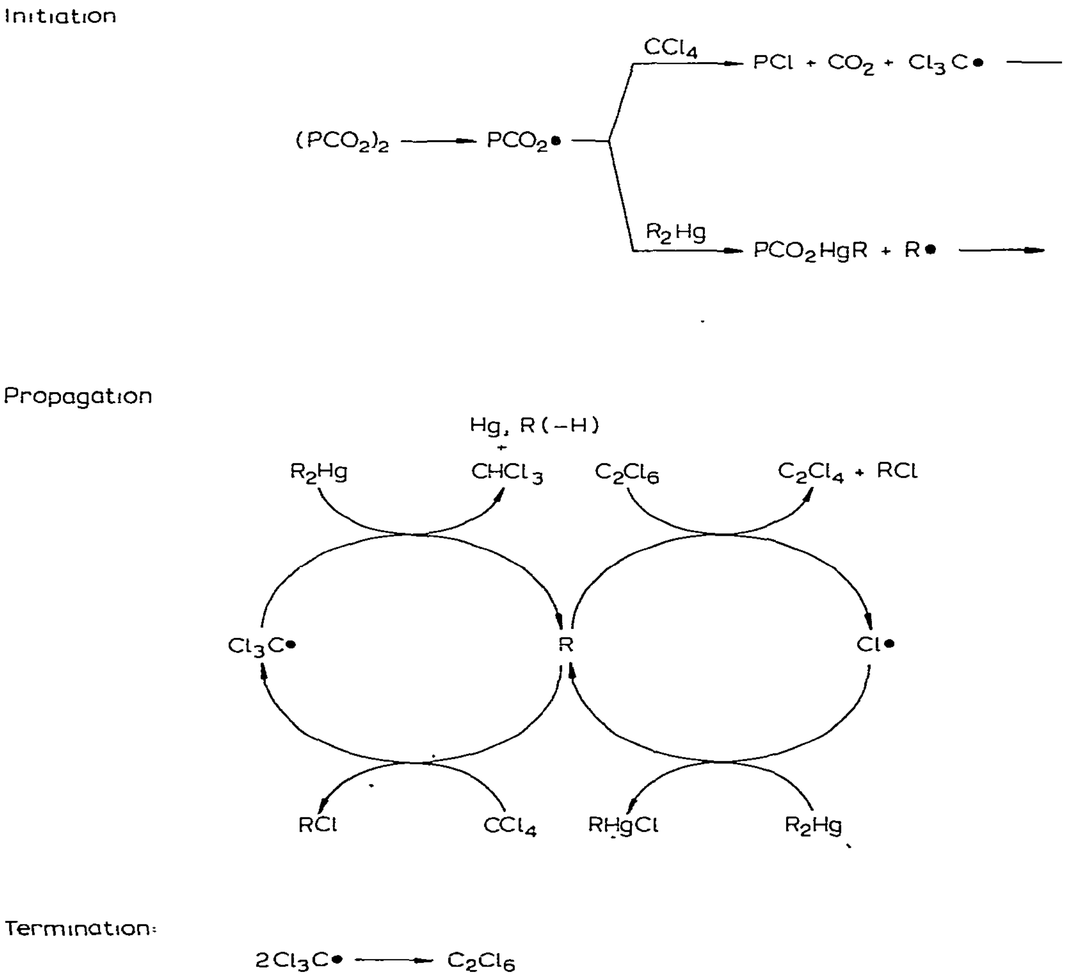
$$RHg\cdot \longrightarrow R\cdot + Hg(O)$$

$$R\cdot + CCl_4 \longrightarrow RCl + Cl_3C\cdot$$

etc.

β-Hydrogen activation toward radical abstraction is very favorable. Thus the β-hydrogen atom in $\underline{H}CMe_2CH_2HgCH_2CMe_3$ is 600 times more reactive than a given hydrogen atom in cyclohexane, a β-hydrogen atom in $CH_3C\underline{H}_2CH_2HgCH_2CMe_3$ about 100 times more reactive, and even the β-hydrogens in $C\underline{H}_3CH_2HgCH_2CMe_3$ 4.4 times more reactive. This translates into a primary:secondary:tertiary H reactivity ratio of 1:22:139. In benzoyl peroxide-initiated reactions of dialkylmercurials in carbon tetrachloride, alkylmercuric chloride and benzoate are formed. It was shown that the chemistry shown in Scheme 2 was involved in their production. In contrast to primary and secondary dialkylmercurials, di-tert-butylmercury reacts spontaneously with carbon tetrachloride in the absence of an initiator (120). A charge-transfer interaction between CCl_4 and $(Me_3C)_2Hg$ was

Scheme 2



shown to be the rate-limiting step:

$$\begin{tikzcd}
R_2Hg + CCl_4 \arrow[r, "E_{CT}"] & {[R_2Hg^{\cdot +}\ \ CCl_4^{\cdot -}]} \arrow[d, "fast"] \\
 & RHgCl + R\cdot + Cl_3C\cdot
\end{tikzcd}$$

$$Cl_3C\cdot + (Me_3C)_2Hg \longrightarrow HCCl_3 + Me_2C{=}CH_2 + Me_3CHg\cdot$$

$$Me_3CHg\cdot \longrightarrow Me_3C\cdot + Hg(0)$$

$$Me_3C\cdot + CCl_4 \longrightarrow Me_3CCl + Cl_3C\cdot$$

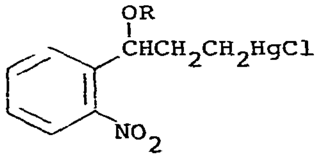
etc.

$Me_3CHgCCl_3$ was shown to be a discrete, transient intermediate:

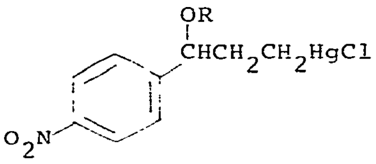
$$Cl_3C\cdot + (Me_3C)_2Hg \xrightarrow{S_H2} Me_3CHgCCl_3 + Me_3C\cdot$$

Pulse radiolysis of benzylic mercurials - $(C_6F_5CH_2)_2Hg$, $(CF_3C_6H_4CH_2)_2Hg$, $(C_6H_5CH_2)_2Hg$ - resulted in formation of the benzylic carbanions, $ArCH_2^-$, and the radicals $ArCH_2Hg\cdot$ (121). Both species were observed spectrophotometrically. In the presence of sodium tetraphenylborate ion pairs, $ArCH_2^-Na^+$, were produced.

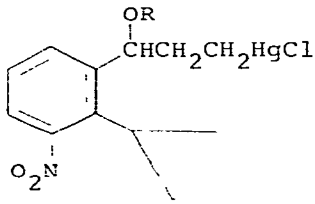
The rate of reductive demercuration of RHgCl ($\longrightarrow$ RH) by sodium borohydride is greatly slowed down by the presence of a nitro substituent (122). Thus the reduction of 60a-63a was exceptionally slow compared to that of similar compounds without a nitro group.



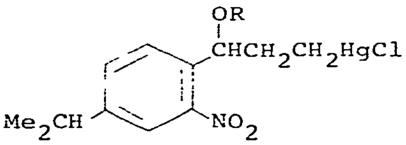
60 a, R = Me
b, R = Ac
c, R = H



61 a, R = Me
b, R = Ac
c, R = H

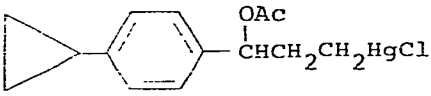


62 a, R = Me
b, R = Ac
c, R = H

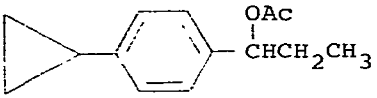


63 a, R = Me
b, R = Ac
c, R = H

Compounds 60b-63b have a carbon-bound acetoxy group which is another potential site for attack by sodium borohydride. Indeed, this reagent does reduce 60b-63b to the alcohols 60c-63c without reaction at the mercury function. These results were explained in terms of an increase in the strength of the Hg-C bond resulting from intermolecular donor-acceptor interaction between the mercury atom and the nitro group. In favor of such a view is the following observation: The reaction of 64 with sodium borohydride gave 65 in 72% yield, along with a 25% recovery of 64. On the other hand, the reaction of 64 with

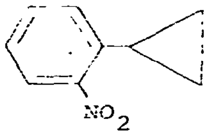


64

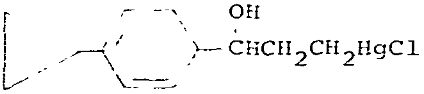


65

sodium borohydride in the presence of <u>66</u> gave alcohol <u>67</u> in 65% yield. The demercuration product was obtained in only 21% yield.



<u>66</u>



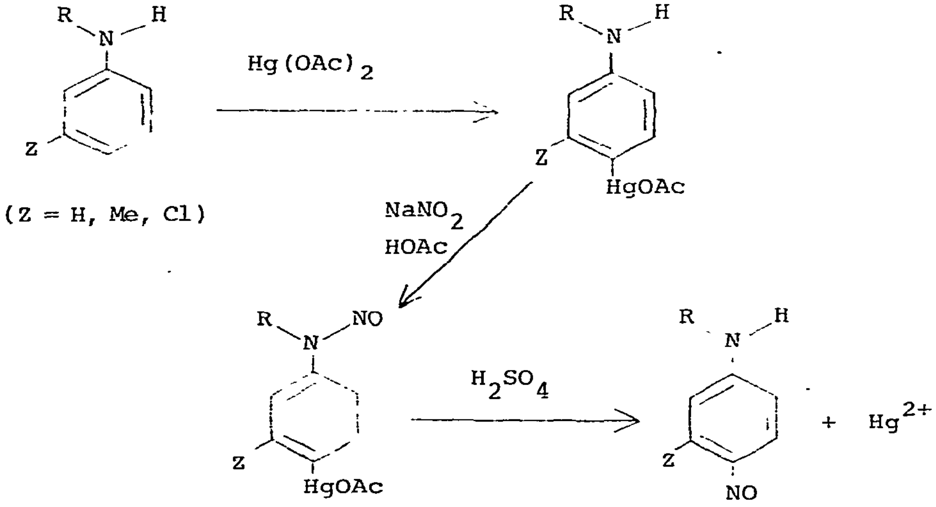
<u>67</u>

Bis(cyclopentadienyl)vanadium(II) was found to reduce organomercuric halides (123):

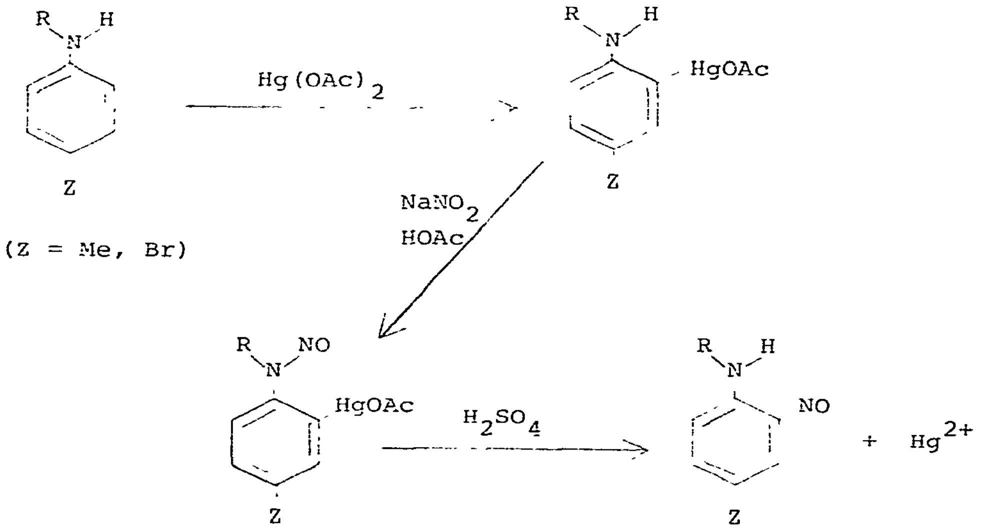
$$2\ (C_5H_5)_2V \quad + \quad 2\ RHgCl \xrightarrow[20^{o}]{\text{hexane}} (C_5H_5)_2VCl + Hg + R_2Hg$$

(R = Ph, Me_3SiCH_2, $(Me_3SiCH_2)_2MeSiCH_2$)

The demercurative rearrangement of some <u>o</u>- and <u>p</u>-mercurated N-nitroso-N-alkylanilines has been studied (124):

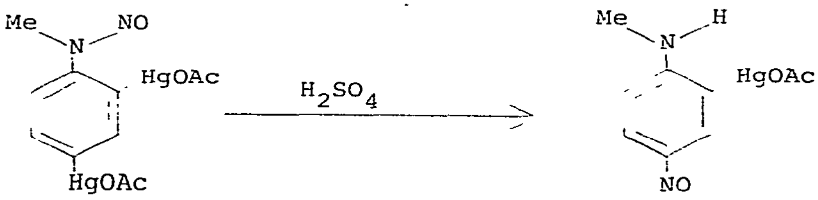


(Z = H, Me, Cl)

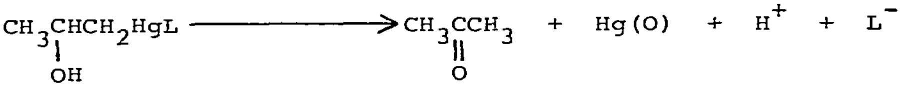


(Z = Me, Br)

An intramolecular process was indicated since these reactions proceeded even in the presence of sulfamic acid or urea which would intercept nitrous acid if it were to be involved as an intermediate. The kinetics of these demercurative rearrangement reactions were studied at varying acid concentrations. The <u>para</u> position is more reactive than the <u>ortho</u> as the reaction below demonstrates. This demercurative rearrangement also could be effected by UV irradiation of the mercurated N-nitrosoanilines in aqueous or alcoholic medium. Quantum yields for such processes were determined.

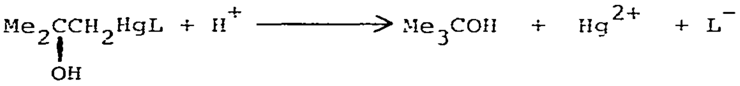


NMR studies of ligand effects on the redox demercuration of β-hydroxypropylmercurials:



$$CH_3\underset{\substack{|\\OH}}{C}HCH_2HgL \longrightarrow CH_3\underset{\substack{\|\\O}}{C}CH_3 + Hg(O) + H^+ + L^-$$

and on the protodemercuration of β-hydroxyisobutylmercurials:



$$\underset{\text{OH}}{\text{Me}_2\text{C}}\text{CH}_2\text{HgL} + \text{H}^+ \longrightarrow \text{Me}_3\text{COH} + \text{Hg}^{2+} + \text{L}^-$$

have been carried out (125). Here L = H_2O or carboxylato, RCO_2^-, with R = CF_3, $CHCl_2$, CH_2Cl, CH_3.

7. MERCURY-FUNCTIONAL MERCURIALS

A. Mercurials with Halogen, Oxygen, Sulfur, Selenium, Tellurium and Nitrogen Substituents.

Equilibria of the reactions of phenylmercuric hydroxide with anions in aqueous solution (pH range 7-10) have been determined (t = 15-45°C) by a potentiometric method (126). For the reaction:

$$\text{PhHgOH} + X^- \overset{K}{\rightleftharpoons} \text{PhHgX} + \text{OH}^-$$

log K varied with X^- as follows: Cl, -4.4; Br, -3.2; I, -0.8; SCN, -3.8; CN, +0.05; NO_2, -6.7; N_3, -4.2; p-$H_2NC_6H_4SO_3$, -6.2.

PhHgX species are more stable than comparable CH_3HgX for all ligands except CN^-. The kinetics of such processes have been studied by the temperature jump relaxation method (127). For a given X^-, both the forward and reverse reactions proceed more rapidly with the PhHg than with the MeHg derivatives. The stability constants of some Hg(II) (128) and Hg(I) (129) carboxylates have been determined by precise potentiometric titration at 25.00°C (3 mol dm^{-3} $NaClO_4$ medium). Unidentate complexes are formed. Table 11 gives results for mercuric carboxylates. Another group has determined stability and hydrolysis rate constants in aqueous solution for mercuric and methylmercuric acetate (130).

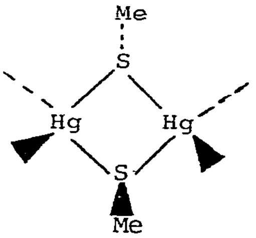
Mercury-sulfur bonding has received continued attention, in part because RHg(II) and Hg(II) tends to bond at sulfur in biological systems.

Mercury(II) and organomercury(II) complexes of thiols and dithiols have been studied (131). The dithiol complexes of type PhHgS~~R~~SHgPh decompose at room temperature in benzene

Table 11. Stability constants of mercury(II) complexes at 25.00°C in a 3 mol dm^{-3} sodium perchlorate medium (128).

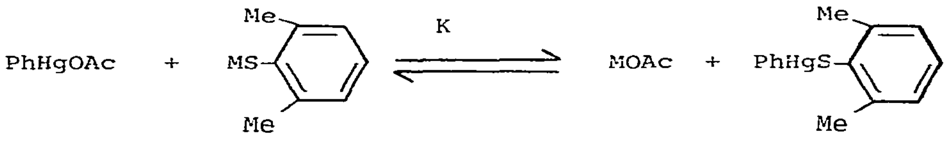
Ligand	log K_1^H	log β_1	log β_2	log $\frac{K_1}{K_2}$
1) Formate	3.907±0.002	3.66±0.01	7.10±0.01	0.22
2) Acetate	5.011±0.002	4.22±0.01	8.45±0.03	-0.01
		4.15±0.01	8.44±0.02	-0.14
3) Propanoate	5.161±0.002	4.33±0.01	8.80±0.03	-0.14
4) Chloroacetate	3.028±0.003	2.95±0.02	5.61±0.02	0.29
5) Cyanoacetate	2.654±0.001	precipitated		
6) Hydroxyacetate	3.923±0.002	3.60±0.01	7.05±0.01	0.15
7) 3-Hydroxybutanoate	4.757±0.004	4.25_5±0.01	8.36±0.01	0.15
8) 4-Hydroxybutanoate	4.985±0.005	4.34±0.01	8.45±0.01	0.23
9) Methoxyacetate	3.743±0.002	3.54±0.02	6.91±0.03	0.17
10) 3-Methoxypropanoate	4.707±0.003	4.24±0.02	8.45±0.03	0.03
		log β_1^*	log β_2^*	
Hydroxide	14.22	-3.44±0.02	-6.24±0.03	-0.64

or methanol, giving diphenylmercury. IR, Raman and proton NMR spectroscopic investigations were carried out on PhHgSR (R = Me, Et, i-Pr, t-Bu, Ph, CH_2CH_2OH) and $Hg(SR)_2$ and dithiol complexes of Hg(II) and RHg(II), and their solution behavior was studied. PhHgSR and $Hg(SR)_2$ (R = Et, t-Bu, Ph) dissolve as monomers in chloroform. The stability constants of the $Hg^{2+}/HOCH_2CH(SH)-CH_2SH$ (BAL) (1:1 and 1:2) complexes have been determined (132). This ligand, although it has only two donor sites, forms a more stable complex with mercuric ion than does EDTA. The formation of dimeric Hg(II) thiolate ions in aqueous solution, derived from MeSHgOAc and its pyridine or 4-methylpyridine complexes, has been described (133). Presumably, double MeS bridging, as in 68, is involved.



68

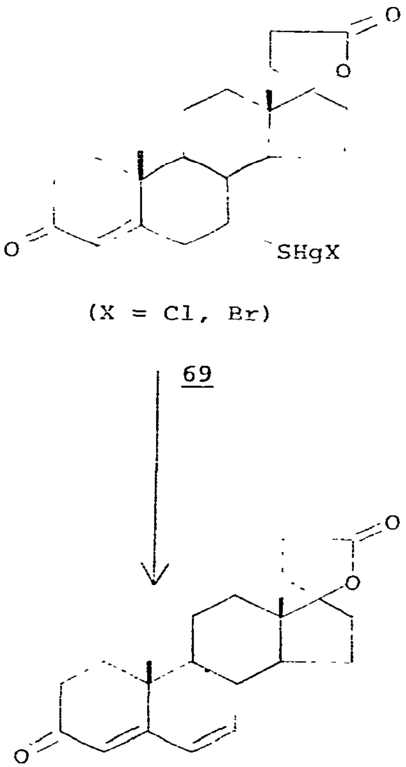
Equilibrium constants have been determined by an NMR procedure for the reaction of phenylmercuric acetate with 2,6-dimethylthiophenol and its triphenyllead and triphenyltin derivatives (134). The results of this study provide another example of the strong affinity of mercury for sulfur bonding:

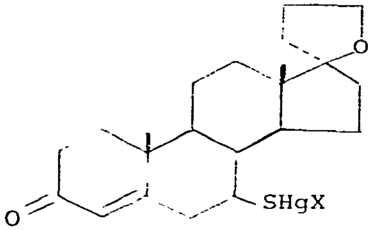


M	Solvent	K
H	$HCCl_3$	>100
Ph_3Sn	$HCCl_3$	>100
Ph_3Pb	$HCCl_3$	5.3±0.5
	$PhNO_2$	9.3±1.0
	C_5H_5N	>100

An interesting solvent effect was observed.

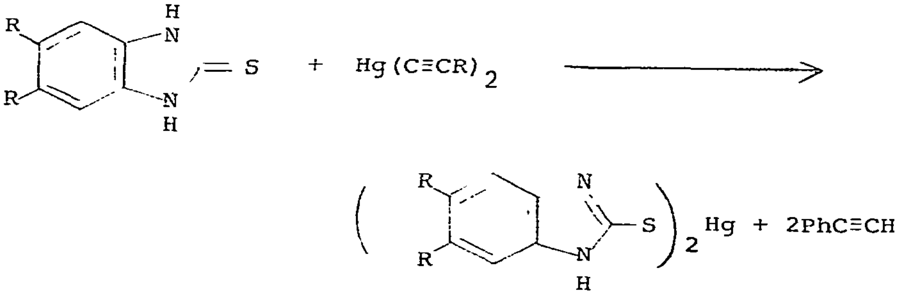
S-Bonded phenylmercury(II) derivatives of L-cysteine and DL-penicillamine have been prepared. Both decompose to give diphenylmercury when their suspensions in benzene are stirred at room temperature (135). Mercury(II) derivatives of some thiosteroids, e.g., 69 and 70, have been reported by Canadian workers (136). They decomposed in solution and in the solid state as shown for 69.





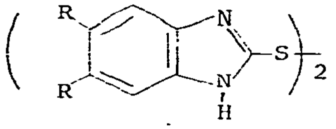
70

Mercury(II) benzimidazole-2-thiolates have been prepared (137):

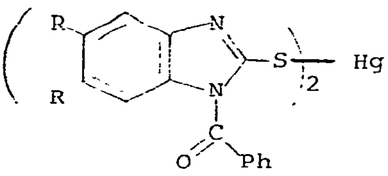


71

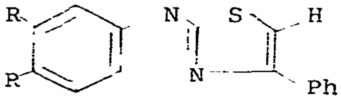
Some reactions of 71 were examined: the action of NaI/I_2 gave disulfide 72; benzoyl chloride produced the N-benzoyl derivative 73 and reaction with $Hg(C\equiv CPh)_2/PhN{=}C{=}S$ gave 74.



72

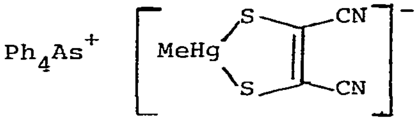


73



74

An anionic MeHg(II) complex of the cis-1,2-dicyanoethylene dithiolate ion, 75, has been characterized (138). The cyclic structure shown is not secure, and it may be that the two Hg-S bonds are not equal in length (as in $MeHgS_2CNEt_2$).



75

The reaction of $C(HgOAc)_4$ or $C(HgO_2CCF_3)_4$ with aqueous methylmercaptan gave $C(HgSMe)_4$, while reaction with aqueous hydrogen sulfide produced CHg_4S_2, a yellow, amorphous solid (139). The latter, very likely a three-dimensional coordination polymer, contains 91.33% Hg, a record for an organomercurial. Both compounds, like all $C(HgX)_4$ species, are very stable thermally, decomposing endothermally between 350 and 400°C. Sulfur, selenium and tellurium-containing mercurate salts have been prepared and studied (140): $[Ph_4P]_2[Hg(EPh)_4]$ (E = S, Se, Te); $[Ph_4P]_3[Hg_2(SePh)_7]$, $[Ph_4P]_5[Hg_3(TePh)_{11}]$. The crystal and molecular structure of $[Ph_4P][Hg(TePh)_3]$ was determined by X-ray diffraction (141). The structure of the anion is shown in Figure 1.

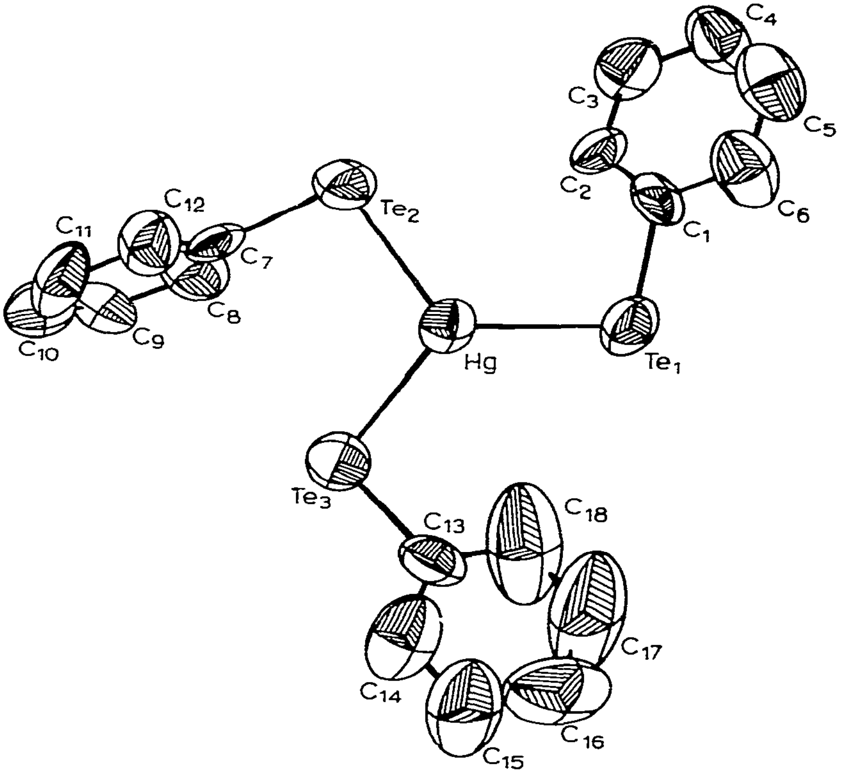
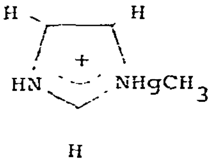


Figure 1. Structure of the Anion in $[Ph_4P][Hg(TePh)_3]$. (U. Behrens, K. Hoffmann and G. Klar., Chem. Ber., 110 (1977) 3672)

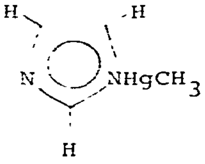
Table 12. Equilibrium Constants for the Methylmercury(II)-Imidazole System (142).

	NMR	pH titration
	Imidazole	
pK_A	7.13	7.10±0.02
Log K_1	6.93±0.04	7.14±0.03
pK_2	9.61±0.2	9.65±0.1
Log K_3	8.26±0.2	8.18±0.1
Log K_4	11.76	11.79±0.1
	N-Methylimidazole	
pK_A	7.18	
Log K_1	6.96	

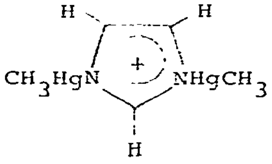
Methylmercury imidazole species which are formed in aqueous solution, 76, 77 and 78, have been investigated (142). Their solution equilibria were determined potentiometrically and their formation constants were determined independently by NMR experiments. Although imidazole has a large relative affinity for MeHg(II), SH functions bind mercury more strongly.



76



77



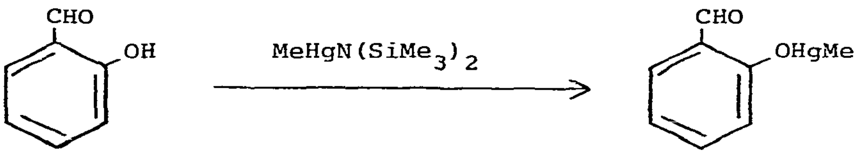
78

$$CH_3Hg^+ + HIm \underset{}{\overset{K_1}{\rightleftharpoons}} CH_3HgHIm^+ \qquad (76)$$

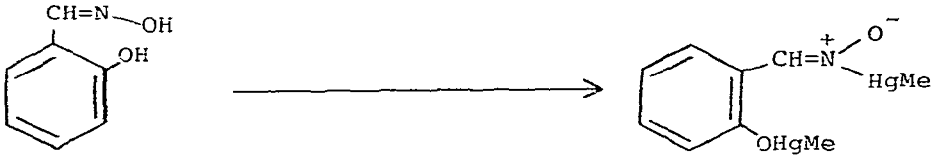
$$CH_3HgHIm^+ \overset{K_2}{\rightleftharpoons} CH_3HgIm + H^+ \qquad (77)$$

$$CH_3Hg^+ + CH_3HgIm \overset{K_3}{\rightleftharpoons} (CH_3Hg)_2Im^+ \qquad (78)$$

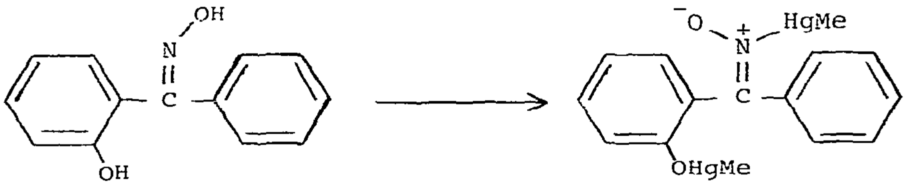
Methylmercury bis(trimethylsilyl)amide and mercury bis-bis-(trimethylsilyl)amide are useful reagents for the introduction of MeHg and Hg functions into molecules by reaction with OH, NH and other protic functionality. Glockling and Mahale (143) have used the former to prepare $CH_3Hg(II)$ derivatives of several oximes and phenols:



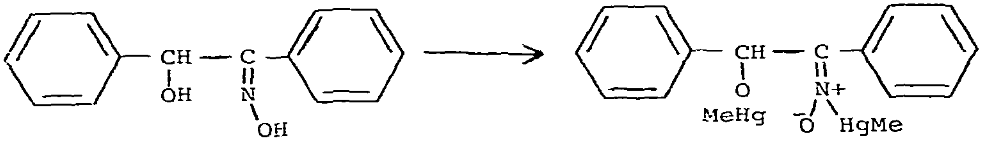
79



80

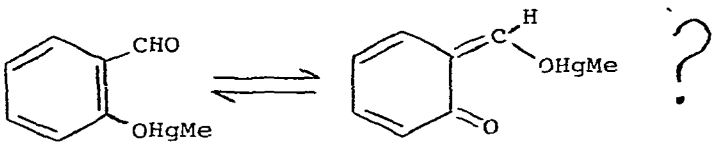


81



82

The nitrone structures 80, 81 and 82 (rather than the alternate O-Hg structures) were considered more probable but remained unproven. No evidence for the benzenoid-quinonoid tautomerism previously claimed (Minkin et al., 1974) for 79 could be detected by UV, IR and NMR. Thus this equilibrium must be called into question.



Reactions of $[(Me_3Si)_2N]_2Hg$ with compounds containing activated C-H bonds provided C-Hg derivatives (144):

$$[(Me_3Si)_2N]_2Hg + 2\ CH_2(CO_2Et)_2 \longrightarrow Hg[CH(CO_2Et)_2]_2 + 2(Me_3Si)_2NH$$

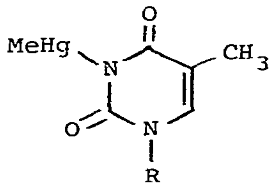
Similar reactions with $CH_2(CN)CO_2Et$, $CH_2(CN)_2$ and $CH_2(COCH_3)_2$ gave $Hg[CH(CN)CO_2Et]_2$, $Hg[CH(CN)_2]_2$ and $Hg[CH(COCH_3)_2]_2$, respectively.

$MeHgN(SiMe_3)_2$ and $Hg[N(SiMe_3)_2]_2$ also react with halides o the Group IV elements, e.g.:

$$Hg[N(SiMe_3)_2]_2 + 2\ HSiCl_3 \longrightarrow 2\ (Me_3Si)_2NSiHCl_2 + HgCl_2$$

The reactivity of the halides decreases in the order: $SnCl_4 > GeCl_4 > SiCl_4$; in the silicon series: $HSiCl_3 > MeHSiCl_2 > SiCl_4 > MeSiCl_3$ (39). Table 13 gives some results.

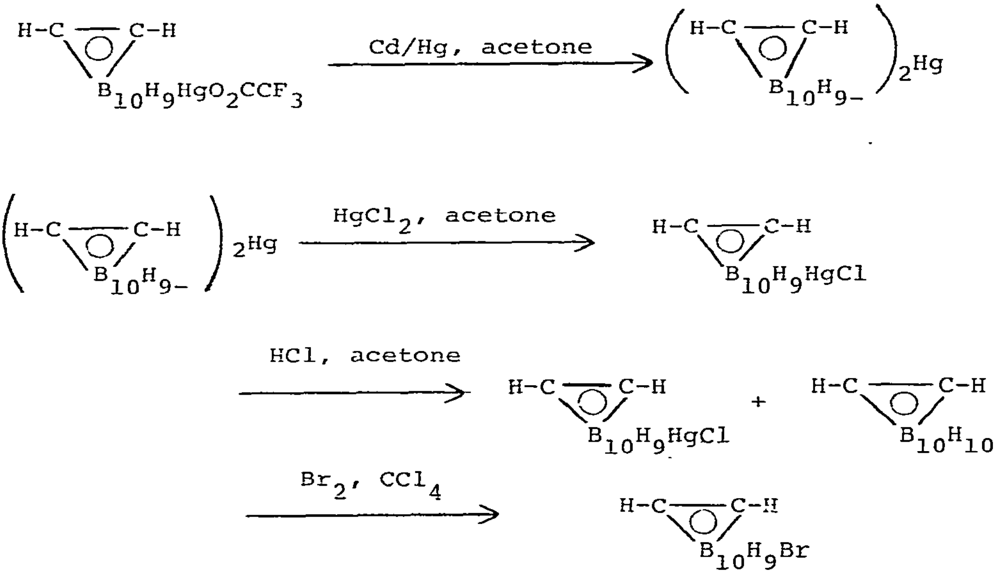
Tobias and his coworkers have reported Raman difference spectroscopic studies on the binding of $CH_3Hg(II)$ to 1-methylthymidine, thymidine-5'-monophosphate, DNA models and native DNA (145). The $CH_3Hg(II)$ derivatives of 1-methylthymidine and dTMP have the N-Hg bonded structure, 83a and b, respectively.



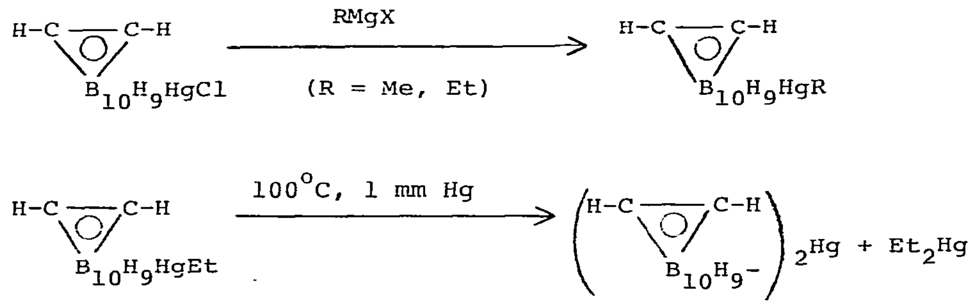
83 a, R = CH_3
b, R = deoxyribose monophosphate

B. B-Mercurated Carboranes

Two Russian groups have reported on the synthesis and reactivity of B-mercurated carboranes (146, 147). Such compounds result on reaction of carboranes with $Hg(O_2CCF_3)_2$ or $Hg(O_2CCH_3)_2/HClO_4$. o- and m-Carborane react with mercuric trifluoroacetate at room temperature, the former exothermally. On the other hand, p-carborane reacts only at higher temperature. Polymercuration is possible (up to five HgX substituents) under forcing conditions. The mercury substituent is introduced predominantly (80-90%) in the 9 position of the o-carboranes, with lesser amounts of 8-substitution, according to brominolysis experiments. *m*-Carborane reacts more selectively, giving the 9-mercurated isomer in 99% yield. Dimercuration gives the 9,10 isomer (98%). Compared with the C-mercurated carboranes which have been investigated extensively (see previous mercury Annual Surveys), the B-mercurated carboranes are more reactive. Thus they react readily with mercuric chloride, bromine and hydrogen chloride at room temperature, e.g., in the *o*-carborane series:



The chloromercuri derivatives may be alkylated. The resulting unsymmetrical diorganomercurials are easily disproportionated:



Polarographic studies of B-mercurated *o*, *m* and *p*-carboranes have been reported (148).

Table 13. Reactions of $MeHgN(SiMe_3)_2$ and $Hg[N(SiMe_3)_2]_2$ with Group IV Halides.

Mercurial	Group IV Halide	Conditions	Product (% Yield)
$MeHgN(SiMe_3)_2$	$SiCl_4$	4d, 160°	$(Me_3Si)_2NSiCl_3$ (71)
	$GeCl_4$	30 min., 20°	$(Me_3Si)_2NGeCl_3$ (91)
	$SnCl_4$	5 min., 20°	$(Me_3Si)_2NSnCl_3$ (89)
	$HSiCl_3$	5 min., 20°	$(Me_3Si)_2NSiHCl_2$ (88)
	$MeHSiCl_2$	4h, 80°	$(Me_3Si)_2NSiMeHCl$ (80)
	$MeSiCl_3$	9d, 160	$(Me_3Si)_2NSiMeCl_2$ (69)
$Hg[N(SiMe_3)_2]_2$	$SiCl_4$	4d, 160°	$(Me_3Si)_2NSiCl_3$ (72)
	$GeCl_4$	30 min., 20°	$(Me_3Si)_2NGeCl_3$ (78)
	$SnCl_4$	5 min., 20°	$(Me_3Si)_2NSnCl_3$ (78)
	$HSiCl_3$	3h, 20°	$(Me_3Si)_2NSiHCl_2$ (75)
	$MeHSiCl_2$	5h, 160°	$(Me_3Si)_2NSiMeHCl$ (67)
	$MeSiCl_3$	10d, 160°	$(Me_3Si)_2NSiMeCl_2$ (63)

C. Mercurials with Group IV Substituents

A new silylmercurial, bis(tri-*tert*-butylsilyl)mercury, has been prepared and its IR, ^1H and ^{13}C NMR spectra have been studied (149):

$$(Me_3C)_2Hg + 2\ (Me_3C)_3SiH \xrightarrow{85^{\circ},\ 24h} [(Me_3C)_3Si]_2Hg + 2C_4H_{10}$$

(greenish crystals)

Perfluorophenylsilanes are much more reluctant to react with di-*tert*-butylmercury, and under the reaction conditions demercuration of the initially formed silylmercurial takes place (144):

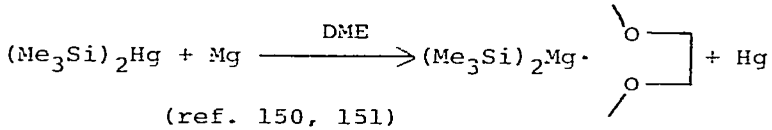
$$\begin{tikzcd}
Me_n(C_6F_5)_{3-n}SiH + (Me_3C)_2Hg \arrow[r, "180-200^{\circ}C"] & Me_n(C_6F_5)_{3-n}SiHgCMe_3 \arrow[d, "+\ C_4H_{10}"] \\
 & Me_n(C_6F_5)_{3-n}SiCMe_3 + Hg
\end{tikzcd}$$

However, when $[(Me_3Si)_2N]_2Hg$ is used in place of di-<u>tert</u>-butylmercury, the synthesis succeeds:

$$2\ Me_2(C_6F_5)SiH + [(Me_3Si)_2N]_2Hg \xrightarrow{270^\circ C} [Me_2(C_6F_5)Si]_2Hg + 2\ (Me_3Si)_2NH$$

$$2\ Et(C_6F_5)_2SiH + [(Me_3Si)_2N]_2Hg \xrightarrow{200^\circ C} [Et(C_6F_5)_2Si]_2Hg + 2\ (Me_3Si)_2NH$$

Bis(trimethylsilyl)mercury has found application in the preparation of $(Me_3Si)_2Mg$ and $(Me_3Si)_3Al$:



$$(Me_3Si)_2Hg + Mg \xrightarrow{DME} (Me_3Si)_2Mg\cdot\left[\begin{matrix}O\\O\end{matrix}\right] + Hg$$

(ref. 150, 151)

$$3\ (Me_3Si)_2Hg + 2\ Al \xrightarrow{THF} (Me_3Si)_3Al\cdot THF + 3\ Hg$$

(ref. 152)

The reaction of bis(trispentafluorophenylgermyl)mercury with praeseodymium in DME at room temperature gave the ionic complex $\{[(C_6F_5)_3Ge]_2Pr\}^+\ \{Hg[Ge(C_6F_5)_3]_3\}^-$, <u>84</u> (153). The reactions of the latter with HCl spoke in favor of the indicated structure:

$$\underline{84} + HCl \xrightarrow[20^\circ]{THF} [(C_6F_5)_3Ge]_2Hg + (C_6F_5)_3GeH + [(C_6F_5)_3Ge]_2PrCl$$

Group IV mercurials are sources of Group IV radicals by way of $Hg\text{-}M^{IV}$ bond homolysis. In a new example, bis(trimethylsilyl)-mercury was found to react with tetraphenyldiphosphine by a UV-induced radical chain mechanism (154):

$$(Me_3Si)_2Hg \xrightarrow{h\nu} 2\ Me_3Si\cdot + Hg(0)$$

$$Me_3Si\cdot + Ph_2P\text{-}PPh_2 \longrightarrow Me_3SiPPh_2 + Ph_2P\cdot$$

$$Ph_2P\cdot + (Me_3Si)_2Hg \longrightarrow Me_3SiPPh_2 + Hg + Me_3Si\cdot$$

etc.

$(Me_3Si)_2Hg$-derived trimethylsilyl radicals apparently reacted with phosphite esters in part by attack at oxygen:

$$Me_3Si\cdot \quad + \quad (RO)_3P \longrightarrow Me_3SiOR \quad + \quad (RO)_2P\cdot$$

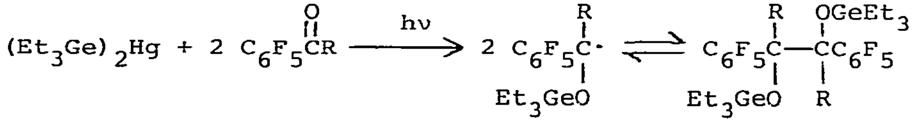
Bis(trimethylsilyl)mercury did not react with $Ph_2P(O)PPh_2$, $Ph_2P(O)P(O)Ph_2$, $Ph_2P(O)CH_2Ph$ or $(EtO)_2P(O)CH_2Ph$ on irradiation

A rather stable stannyl radical has been generated from a mercurial precursor and its ESR spectrum was studied (155):

$$[(PhCMe_2CH_2)_3Sn]_2Hg \xrightarrow{h\nu} 2\ (PhCMe_2CH_2)_3Sn\cdot \quad + \quad Hg(O)$$

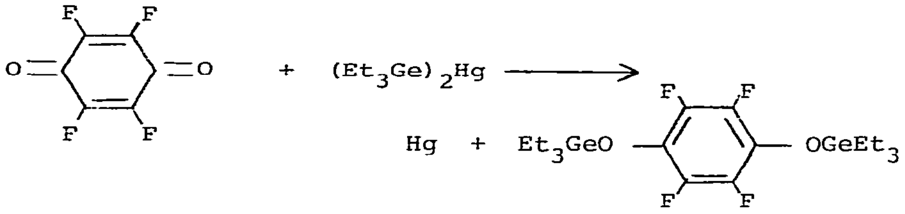
The stannylmercurial, yellow crystals with mp 114°C, was prepared by reaction of the hydride, $(PhCMe_2CH_2)_3SnH$, with di-tert-butyl-mercury.

The UV-induced reaction of bis(trimethylgermyl)mercury with perfluorinated ketones ($C_6F_5C(O)CF_3$, $(C_6F_5)_2CO$, $C_6F_5C(O)-C_6H_5$) also is a free radical process (156):

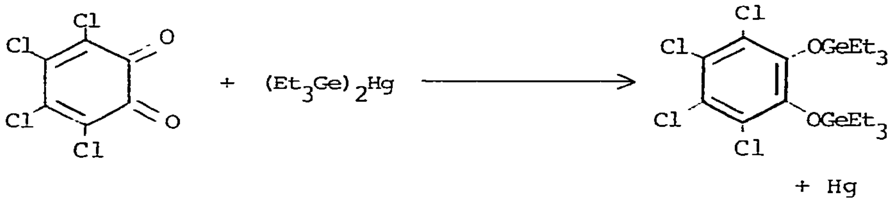


$$(Et_3Ge)_2Hg + 2\ C_6F_5\overset{\overset{O}{\|}}{C}R \xrightarrow{h\nu} 2\ C_6F_5\underset{Et_3GeO}{\overset{R}{C}}\cdot \rightleftharpoons C_6F_5\underset{Et_3GeO}{\overset{R}{C}}-\underset{R}{\overset{OGeEt_3}{C}}C_6F_5$$

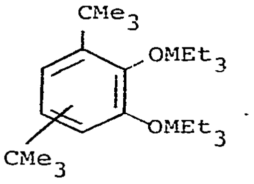
The initially formed radicals, which may be observed by ESR, dimerize. Fluoranil reacts with bis(triethylgermyl)mercury at -78° even when the system is not irradiated:



o-Chloranil reacts with bis(triethylgermyl)mercury at -80°C in similar fashion (157):



EPR showed radical intermediates to be involved. 3,5- and 3,6-Di-tert-butyl-1,2-benzoquinone reacted similarly with $(Et_3Si)_2Hg$ and $(Et_3Ge)_2Hg$, giving 85.



(M = Si, Ge)

85

Methyl(trimethylsilyl)mercury and bis(trimethylsilyl)mercury react with Group IV halides (39):

$$MeHgSiMe_3 + SiCl_4 \xrightarrow{160^\circ C,\ 2\ weeks} Me_3SiCl\ (89\%) + MeSiCl\ (74\%) + Hg\ (100\%)$$

$$MeHgSiMe_3 + GeCl_4 \xrightarrow{20^\circ C,\ 30\ min.} Me_3SiCl\ (93\%) + MeGeCl_3\ (79\%) + Hg\ (92\%)$$

$$MeHgSiMe_3 + SnCl_4 \xrightarrow{20^\circ C,\ 5\ min.} Me_3SiCl\ (100\%) + MeSnCl_3\ (71\%) + Hg\ (95\%)$$

$$(Me_3Si)_2Hg + SiCl_4 \xrightarrow{160^\circ C,\ 2\ weeks} Me_3SiCl\ (100\%) + Me_3SiSiCl_3\ (62\%) + Hg\ (91\%)$$

$$(Me_3Si)_2Hg + GeCl_4 \xrightarrow{20^\circ C,\ 30\ min.} Me_3SiCl\ (100\%) + Me_3SiGeCl_3\ (47\%) + Ge_2Cl_6\ (48\%) + Si_2Me_6\ (43\%) + Hg$$

$$(Me_3Si)_2Hg + SnCl_4 \xrightarrow{20^\circ C,\ 5\ min.} Me_3SiCl\ (85\%) + SnCl_2\ (89\%) + Hg$$

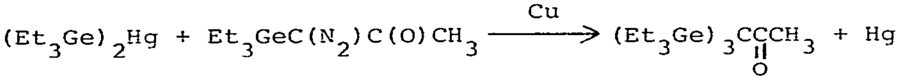
These reactions are believed to proceed via intermediate mercurials, $\mathrm{MeHgMCl_3}$ and $\mathrm{Me_3SiHgMCl_3}$ (M = Si, Ge, Sn), which then undergo demercuration under the reaction conditions.

Further Group IV mercurial/mercurated diazoalkane reaction have been reported by Vyazankin and his coworkers (158):

$$\mathrm{(Et_3M)_2SiHg + Hg[C(N_2)C(O)R]_2 \longrightarrow 2\ Et_3MHgC(N_2)C(O)R}$$

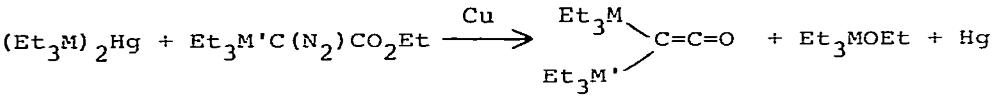
(M = Si, Ge; R = Me, Et, Ph, OMe, OEt)

$$\mathrm{2\ Et_3MHgC(N_2)C(O)R \longrightarrow 2\ Et_3MC(N_2)C(O)R + 2\ Hg}$$



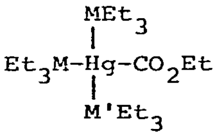
$$\mathrm{(Et_3Ge)_2Hg + Et_3GeC(N_2)C(O)CH_3 \xrightarrow{Cu} (Et_3Ge)_3C\underset{\underset{O}{\|}}{C}CH_3 + Hg}$$

The latter reaction involves (formal) insertion of the carbene $\mathrm{Et_3GeCC(O)CH_3}$ into the Ge-Hg bond. Similar reactions with diazo esters result in the formation of ketenes (159):



(M, M' = Si, Si
Ge, Si
Ge, Ge
Ge, Sn)

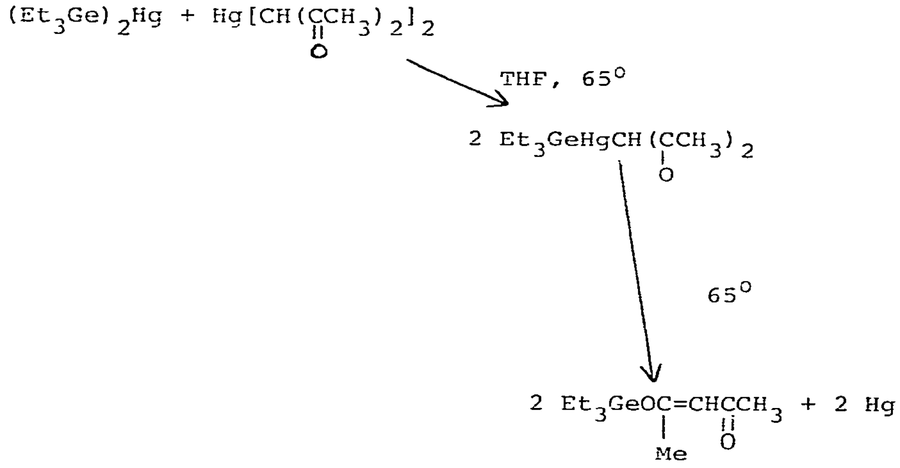
In this reaction a labile intermediate, 86, the product of (formal) $\mathrm{Et_3M'CCO_2Et}$ insertion into the M-Hg bond, very likely is involved. Reactions of bis(triethylgermyl)mercury with mercury derivatives of acetylacetone, diethyl malonate and ethyl



$$\mathrm{Et_3M{-}\underset{\underset{M'Et_3}{|}}{\overset{\overset{MEt_3}{|}}{Hg}}{-}CO_2Et}$$

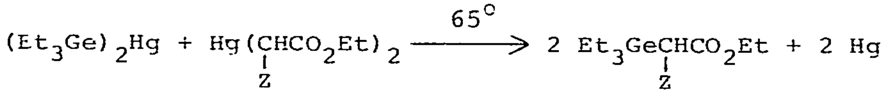
86

cyanocetate resulted in redistribution and subsequent demercuration (144):



$$(Et_3Ge)_2Hg + Hg[CH(\underset{O}{\underset{\|}{C}}CH_3)_2]_2 \xrightarrow{THF,\ 65^{\circ}} 2\ Et_3GeHgCH(\underset{O}{\underset{|}{C}}CH_3)_2 \xrightarrow{65^{\circ}} 2\ Et_3GeO\underset{Me}{\underset{|}{C}}=CH\underset{O}{\underset{\|}{C}}CH_3 + 2\ Hg$$

Similarly:



$$(Et_3Ge)_2Hg + Hg(\underset{Z}{\underset{|}{C}}HCO_2Et)_2 \xrightarrow{65^{\circ}} 2\ Et_3Ge\underset{Z}{\underset{|}{C}}HCO_2Et + 2\ Hg$$

$(Z = CO_2Et,\ CN)$

$$(Et_3Ge)_2Hg + Hg(CH_2CN)_2 \xrightarrow{benzene} 2\ Et_3GeCH_2CN + 2\ Hg$$

$$(Et_3Ge)_2Hg + ClHgCH_2CN \xrightarrow{THF} Et_3GeCH_2CN + Et_3GeCl + 2\ Hg$$

The reaction of potassium cyanide, in the presence or the absence of a crown ether, with bis(triethylgermyl)mercury in THF or acetonitrile at room temperature results in formation of hexaethyldigermane and elemental mercury (160). The reaction course shown below was postulated.

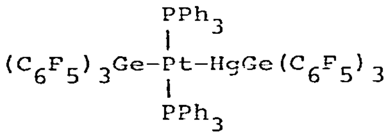
$$(Et_3Ge)_2Hg + CN^- \longrightarrow Et_3GeCN + Hg + Et_3Ge^-$$

$$Et_3Ge^- + Et_3GeCN \longrightarrow Et_3Ge\text{-}GeEt_3 + CN^-$$

When such a reaction was carried out with $(Et_3Si)_2Hg$, the silylmercurial, rather than Et_3SiCN, reacted with the triethylsilyl anion which is generated, to give silylmercurates of the type $K_n[Hg(SiEt_3)_{n+2}]$ (n = 1,2), and Et_3SiCN could be isolated.

$EtHgGeEt_3$ reacted with KCN to give Et_6Ge_2, diethylmercury and elemental mercury.

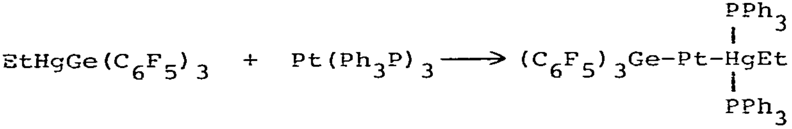
Bis[tris(pentafluorophenyl)germyl]mercury reacts readily with $Pt(Ph_3P)_3$ to give complexes of type 87 (161).



$$(C_6F_5)_3Ge\text{-}\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pt}}\text{-}HgGe(C_6F_5)_3$$

87

Also reported were:



$$EtHgGe(C_6F_5)_3 \ + \ Pt(Ph_3P)_3 \longrightarrow (C_6F_5)_3Ge\text{-}\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pt}}\text{-}HgEt$$

$$[(C_6F_5)_3Sn]_2Hg \ + \ Pt(Ph_3P)_3 \longrightarrow (C_6F_5)_3Sn\text{-}\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pt}}\text{-}HgSn(C_6F_5)_3$$

These complexes are air-stable. They are, however, photolabile and react with bromine, hydrogen chloride and hydrogen.

$$(C_6F_5)_3GePt(Ph_3P)_2HgGe(C_6F_5)_3 \ + \ 2\ Br_2 \xrightarrow{\text{benzene}}$$

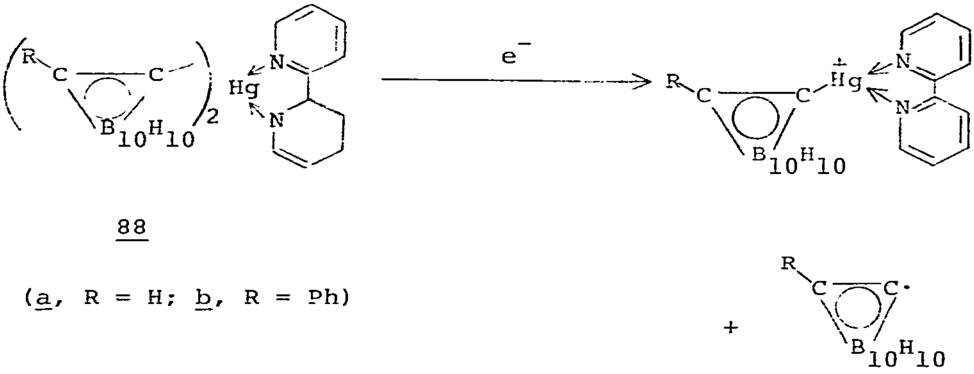
$$(C_6F_5)_3GePt(Ph_3P)_2Br \ + \ (C_6F_5)_3GeBr \ + \ Hg_2Br_2$$

8. COMPLEXES OF ORGANOMERCURIALS

Graddon and Mondal have investigated the thermodynamics of the interactions of Lewis bases with organomercuric halides (162). Alkylmercuric halides form reasonably stable complexes with bidentate bases (o-phen, TMEDA) in benzene solution, but the stability of the complexes which are formed in benzene between RHgX and heterocyclic bases is very low. On the other hand, more stable, dimeric adducts, $[RHgX{\cdot}PBu_3]_2$, are formed with tri-n-butylphosphine. Stronger complexes could be obtained with trichloromethylmercurials, CCl_3HgCl and $(CCl_3)_2Hg$, and Lewis bases such as nitrogen bases, tetrahydrothiophene and pyridine N-oxide. However, in reactions of these mercurials with phosphines secondary processes intrude: symmetrization in the case of CCl_3HgCl and reduction to Hg(O) in the case of $(CCl_3)_2Hg$. 1:1 Adducts of 1,10-phenanthroline with $Hg(CN)_2$, PhHgCN, $PhHgC\equiv CH$, $PhHgC\equiv CMe$, $Hg(C\equiv CMe)_2$, $PhHgC\equiv CCH_2Cl$, $Hg(C\equiv CCH_2Cl)_2$, $PhHgC\equiv CPh$ and $Hg(C\equiv CPh)_2$ have been prepared and studied by IR spectroscopy (163). The phenyl(alkynyl)mercurials were obtained by a redistribution reaction:

$$Ph_2Hg + Hg(C\equiv CR)_2 \xrightarrow{\text{benzene, reflux}} 2\ PhHgC\equiv CR$$

A Swiss group has investigated the interaction of methylmercuric hydroxide with 1,10-phenanthroline, as well as with 2,2'-bipyridine, terpyridine and pyridine-2-azo-4-dimethylaniline (kinetics using the temperature jump relaxation method) (164). Chelate complexes are formed; their reactions with hydroxide ion to CH_3HgOH are extremely rapid. 2,2'-Bipyridine complexes of bis(*o*-phenylcarboranyl)mercury (88b) can be easily oxidized on a stationary platinum microelectrode (165):

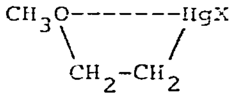


88

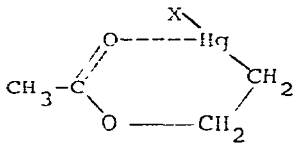
(a, R = H; b, R = Ph)

The uncomplexed carboranylmercurials, however, are resistant to oxidation under these conditions.

A dipole moment study produced data which were interpreted in terms of weak intramolecular coordination between mercury and oxygen functionality in 89 and 90 in benzene medium (166). In ethyl acetate, only 90 gave evidence of such an interaction. No hint of intramolecular coordination was found in dipole moment studies of $CF_3CH_2CH_2HgX$ and $(O_2N)_3CCH_2CH_2HgX$ compounds.



89



90

Bromide ion complexes of cyclopentadienylmercuric bromide are readily formed in aqueous solution (116):

$$C_5H_5HgBr + Br^- \xrightarrow{K\sim 750} C_5H_5HgBr_2^-$$

$$C_5H_5HgBr_2^- + Br^- \xrightarrow{K<100} C_5H_5HgBr_3^{2-}$$

Evidence even was obtained for the formation of $C_5H_5HgBr_4^{3-}$. Cyclopentadienylmercuric bromide thus appears to be a stronger Lewis acid with respect to bromide ion than any other RHgBr, stronger even than mercuric bromide, perhaps as a result of the pronounced anionic character of the cyclopentadienyl substituent.

Finally, complexes which are formed between benzylmercuric halides and bis(cyclopentadienyl)zirconium dihalides should be mentioned. The nature of these complexes remains unknown (167).

$$(\pi\text{-}C_5H_5)_2ZrX_2 + 3\ PhCH_2HgX \xrightarrow{CCl_4,\ 50^oC} (\pi\text{-}C_5H_5)_2ZrX_2\cdot 3PhCH_2HgX$$

9. STRUCTURAL STUDIES OF ORGANOMERCURIALS AND RELATED MERCURY COMPOUNDS

A refinement of the crystal structure of diphenylmercury has been reported (168). Figure 2 shows the structure. The C-Hg bond distance is 2.085(7) Å. Also determined have been the crystal and molecular structures of $[(Me_3Si)_3C]_2Hg$ (10) (Figure 3); d(C-Hg) = 2.142(4) Å, and of $(CF_3)_2Hg$ (169) (Figure 4); d(C-Hg) = 2.118 Å. In the crystal of $(CF_3)_2Hg$, which is made up of discrete, monomeric molecules, there are six intermolec-

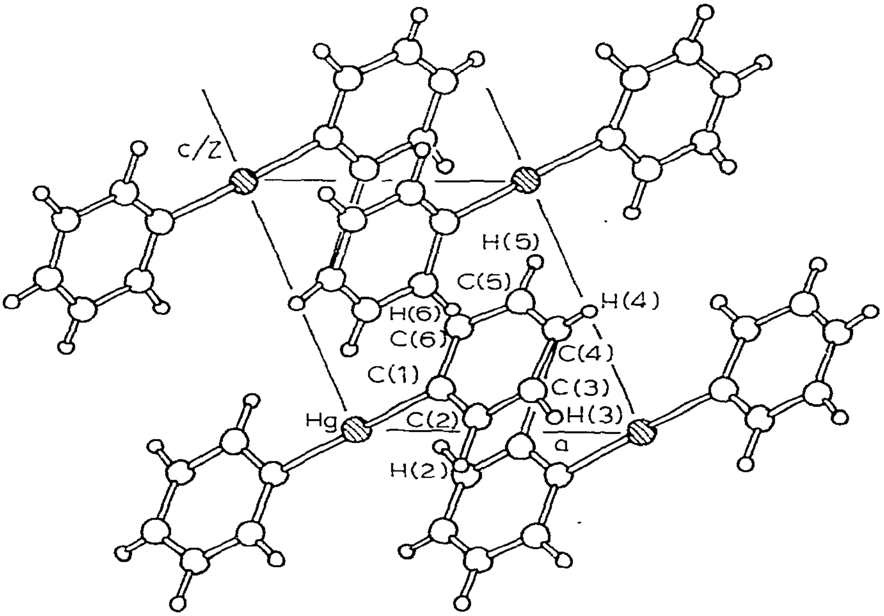


Figure 2. Crystal Structure of Diphenylmercury, viewed along b̲. (from D. Grdenić, B. Kamenar and A. Nagl, Acta Cryst. B, 33 (1977) 587)

ular Hg-F contacts of 3.181(7) Å per mercury atom. This distance is long, but the authors consider that "interactions between nonbonding fluorine 2p orbitals and unfilled mercury 6p orbitals and/or coulombic attraction between oppositely charged fluorine and mercury atoms appear to be significant." This view finds support in details of the vibrational spectrum and the high (163°C) melting point (relative to $(CH_3)_2Hg$).

The crystal structures of two mercurated diazoalkanes, $Hg[C(N_2)CO_2C_2H_5]_2$ (170) and $Me_3CHgC(N_2)CO_2C_2H_5$ (171), have been determined by X-ray diffraction (Figures 5 and 6). Russian workers have reported the crystal and molecular structure of N-phenylmercuri-N,N'-di-p-tolylformamidine (172) (Figure 7). This compound, as well as others of this class, were prepared

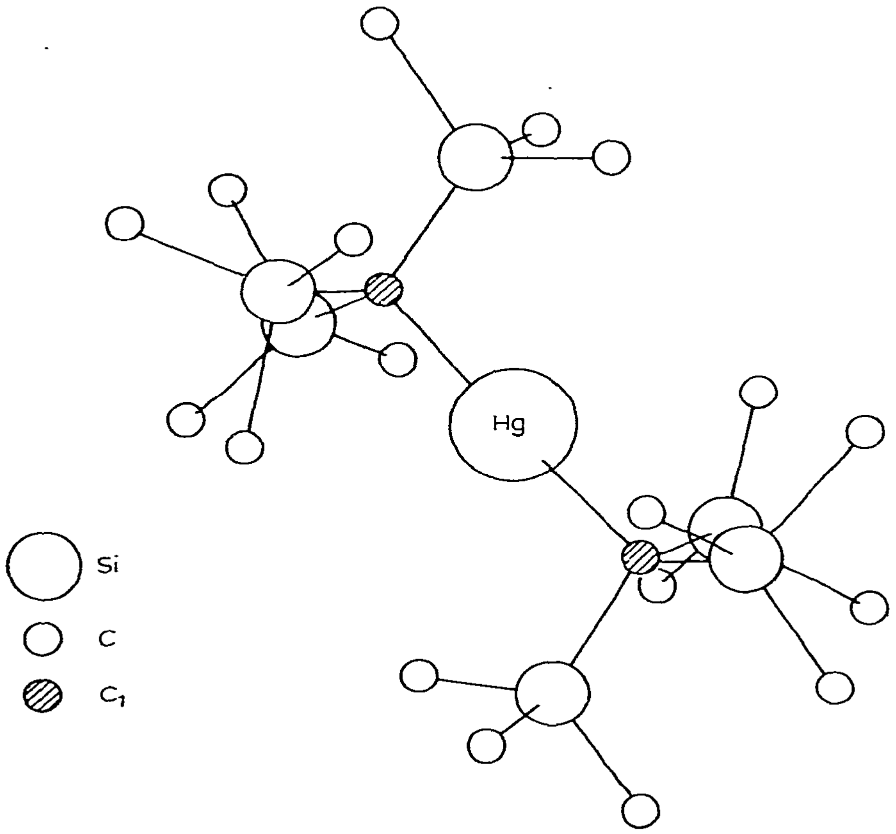


Figure 3. Crystal Structure of $[(Me_3Si)_3C]_2Hg$ (from F. Glockling, N. S. Hosmane, V. B. Mahale, J. J. Swindall, L. Magos and T. J. King, J. Chem. Res. (S) (1977) 116)

as shown below. In the crystal there are two independent molecules which have different structures.

$$\mathrm{PhHgOH + ArNH{-}CH{=}NAr' \longrightarrow ArN(HgPh){-}CH{=}NAr' + H_2O}$$

Two biologically important organomercurials have been e amined by X-ray diffraction: (DL-methioninato)methylmercury

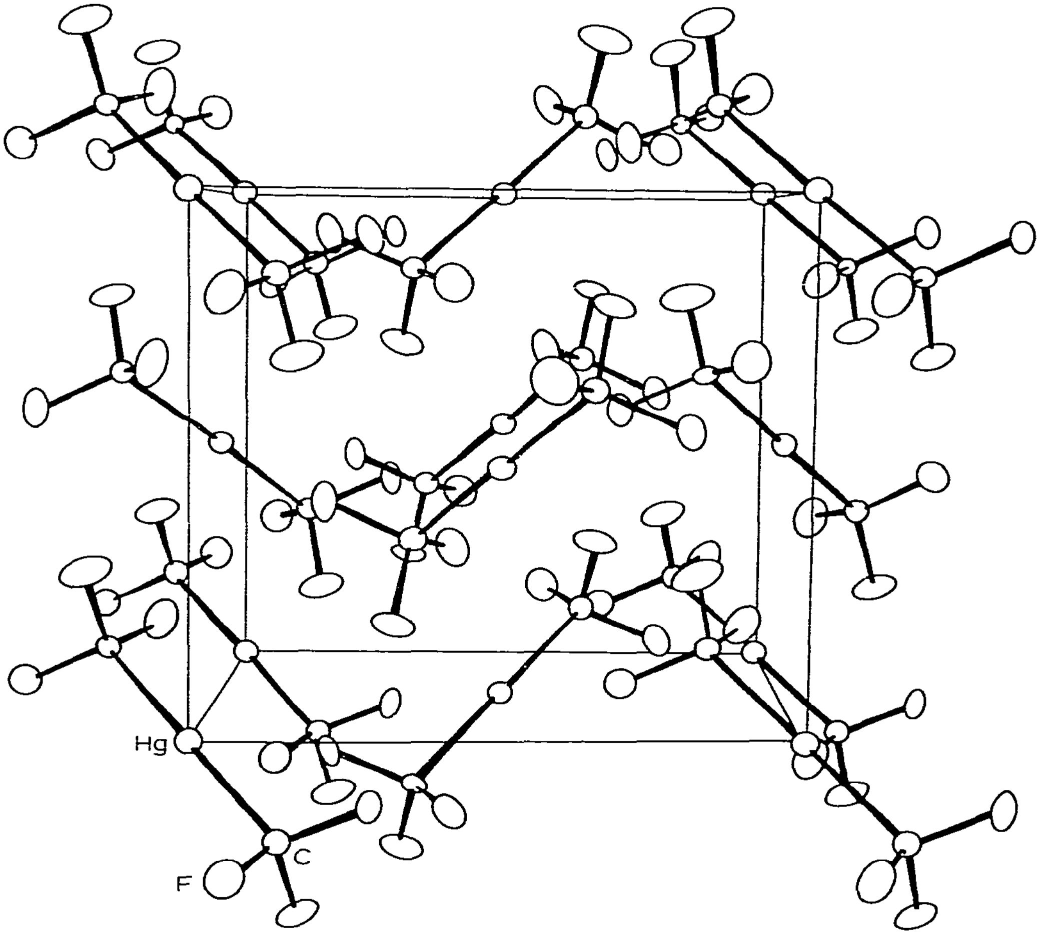


Figure 4. Crystal Structure of Bis(trifluoromethyl)mercury. (from D. J. Brauer, H. Bürger and R. Eujen, J. Organometal. Chem., 135 (1977) 281)

(Figure 8) (173) and (DL-penicillaminato)methylmercury (Figure 9) and μ-DL-penicillaminato-bis(methylmercury) (Figure 10) (174). In all three compounds there appear to be weak interactions between mercury atoms and nearby oxygen or sulfur atoms.

The crystal and molecular structure of 3-triphenylphosphino-3-mercura-1,2-dicarbadodecaborane has been determined (Figure 11) (175). The mercury atom is bonded to boron, not to carbon.

(Continued on p. 228)

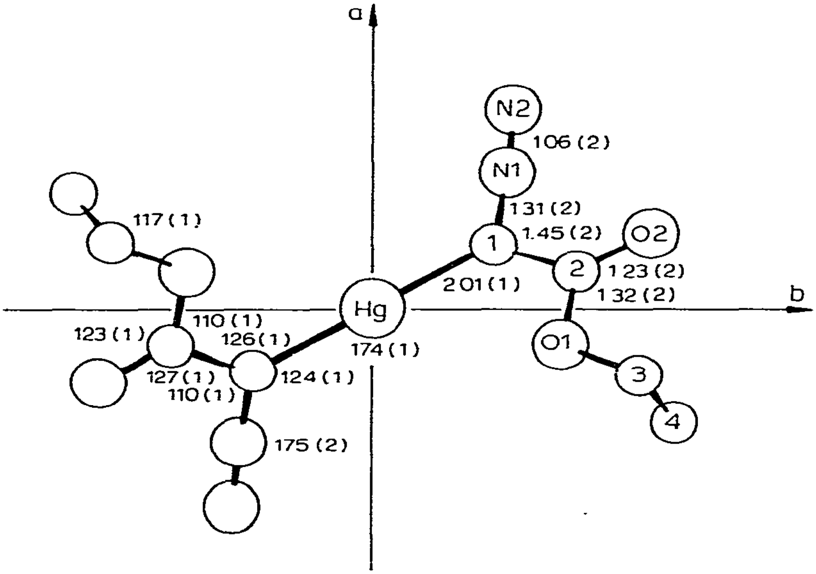


Figure 5. Molecular Structure of $Hg[C(N_2)CO_2C_2H_5]_2$. (from R. A. Smith, M. Torres and O. P. Strausz, Can. J. Chem., 55 (1977) 3527)

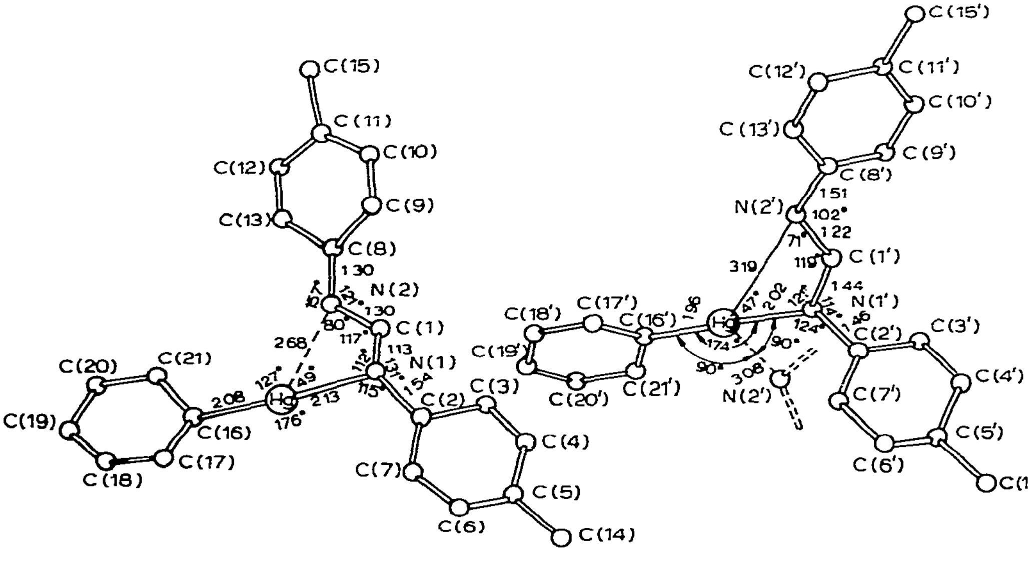


Figure 7. Structure of the crystallographically independent molecules of N-Phenylmercuri-N,N'-di-p-tolyformamidine. (from L. G. Kuz'mina, N. G. Bokii, Yu. T. Struchkov, V. I. Minkin, L. P. Olekhnovich and I. E. Mikhailov, Zh. Strukt. Khim., 18 (1977) 122)

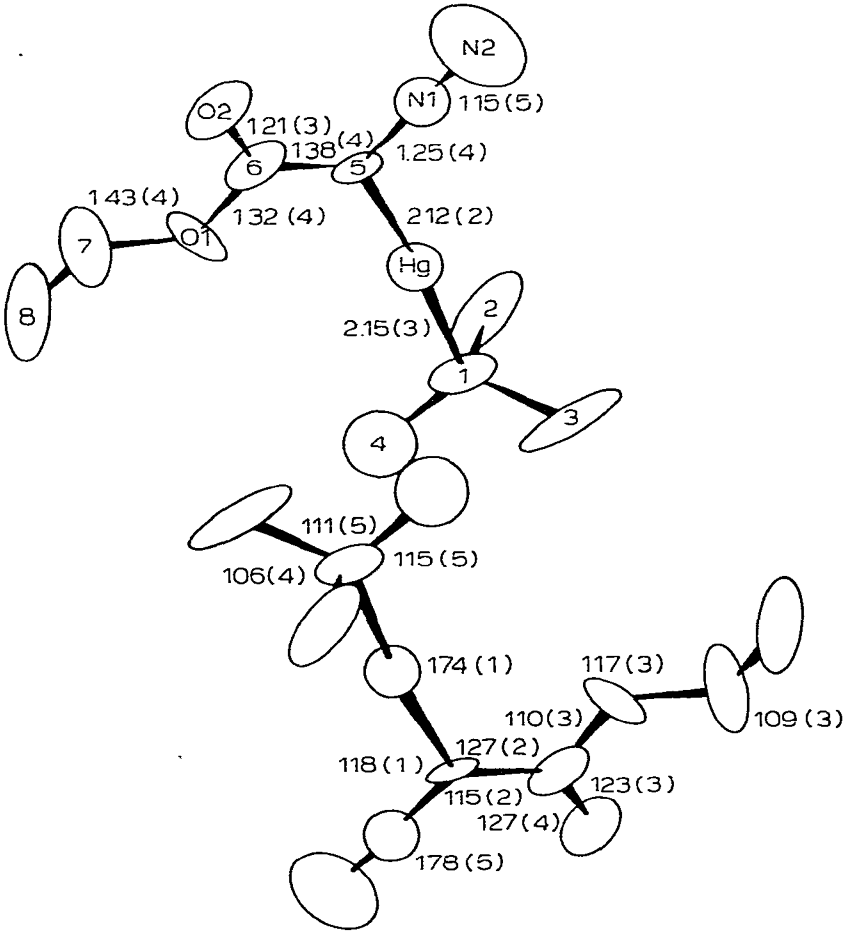


Figure 6. Molecular Structure of $Me_3CHgC(N_2)CO_2C_2H_5$.
(from R. A. Smith, M. Torres and O. P. Strausz, Can. J. Chem., 55 (1977) 2752)

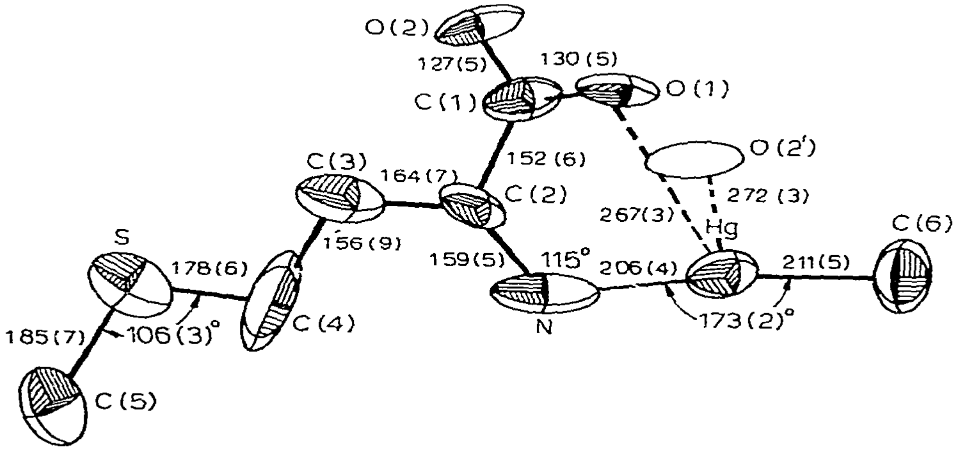


Figure 8. Molecular Structure of (DL-Methionato)methylmercury (from Y.-S. Wong, A. J. Carty and P. C. Chieh, J. Chem. Soc., Dalton Trans. (1977) 1157)

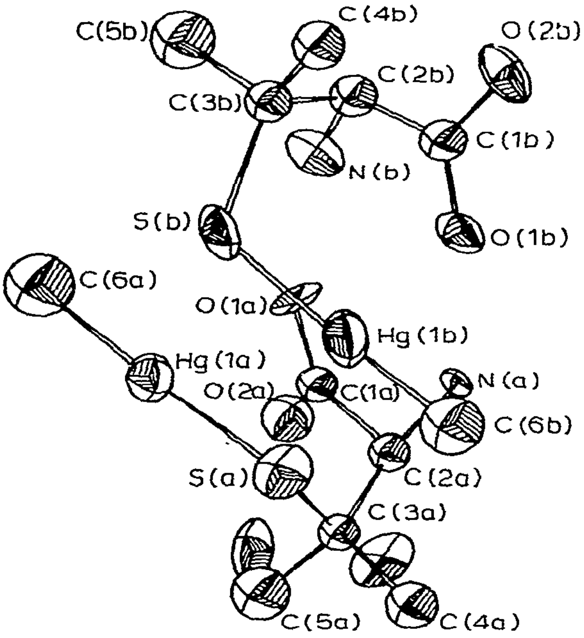


Figure 9. Molecular Structure of (DL-Penicilliminato)methylmercury Monohydrate. (The two unlabelled atoms are oxygen atoms of water of crystallization.) (from Y.-S. Wong, A. J. Carty and P. C. Chieh, J. Chem. Soc., Dalton Trans. (1977) 1801)

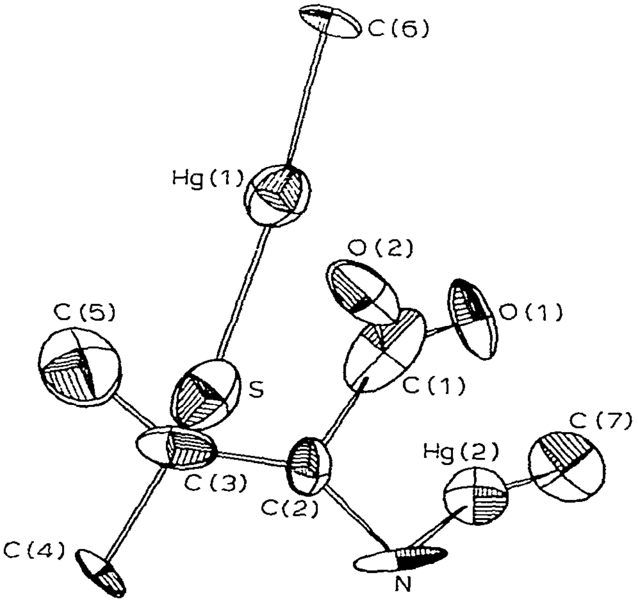


Figure 10. Molecular Structure of u-DL-Penicillaminato-bis(methylmercury).
(from Y.-S. Wong, A. J. Carty and P. C. Chieh, J. Chem. Soc., Dalton Trans. (1977) 1801)

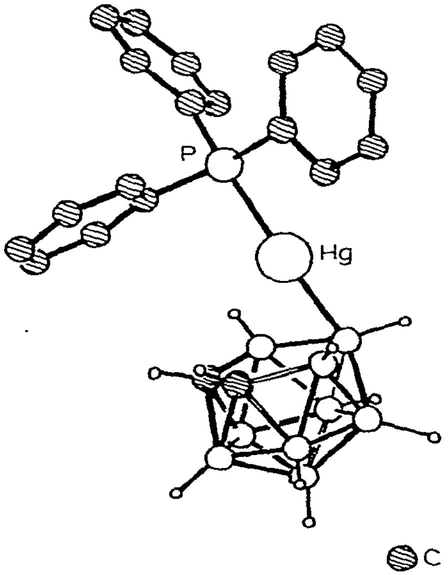


Figure 11. Molecular Structure of 3-Triphenylphosphino-3-mercura-1,2-dicarbadodecaborane.
(from H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, J. Chem. Soc., Chem. Comm. (1977) 737)

10. SPECTROSCOPIC STUDIES OF ORGANOMERCURIALS

A. Vibrational Spectroscopy

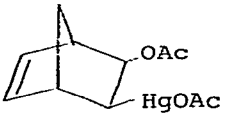
The vibrational spectra of gaseous, liquid and solid dimethylmercury (176), of gaseous and solid bis(trifluoromethyl)-mercury and of its solution in acetonitrile (169), of phenylmercuric chloride, bromide and iodide and of diphenylmercury (177) and the IR spectrum of 2- and 3-chloromercurifuran in carbon disulfide (178) have been reported. Japanese workers have studied solvent effects on the Raman spectra of the mercuric halides (179).

B. Electronic Absorption Spectroscopy

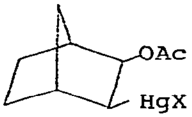
The electronic absorption spectra of the bis-π-tricarbonylchromium derivatives of some diarylmercurials revealed a linear relationship between the extinction coefficients of the longer wave length absorption band and the σ_p^+ constants of the substituents in the phenyl groups (180). Indian workers have reported studies of the UV spectra of o- and p-halomercuriphenols (181) and Russian workers have investigated the electronic absorption spectra of $(Et_3Si)_2Hg$ and $(Et_3Ge)_2Hg$ (182).

C. Nuclear Magnetic Resonance Spectroscopy

^{1}H and ^{13}C NMR studies have been carried out on $MeCH(OH)-CH_2HgCl$ and $Me_2C(OH)CH_2HgY$ (Y = OAc, Cl, Br, SCN, I, CN), with emphasis on nuclear spin-spin coupling constants (183). ^{13}C NMR studies have been reported on $[(CH_2{=}CH(CH_2)_n]_2Hg$ (n = 2,3,4) and di-n-butylmercury. One, two and three-bond ^{199}Hg-^{13}C coupling was observed (184). ^{13}C NMR studies also were carried out on mercurated diazoalkanes ($MeHgC(N_2)CO_2Et$, $Hg[C(N_2)CO_2Et]_2$, $(MeHg)_2CN_2$) (185), oxymercuration products of norbornene derivatives, 91, 92, 93 and 94,(186) and of $(Me_3Si)_2Hg$, $(Et_3Si)_2Hg$, $[(Me_3C)_3Si]_2Hg$ and $(Me_3C)_2Hg$ (187).

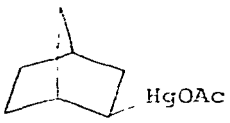


91

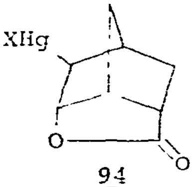


92

(X = OAc, Cl)



93



94

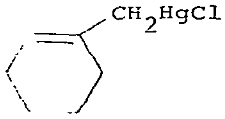
(X = OAc, Cl)

Detailed studies of the NMR spectra of cyclohexylmercurials (RHgOAc, RHgCN, RHgPh, R_2Hg, trans-4-MeRHgOAc; R = cyclo-C_6H_{11}) have been reported by Barron, Doddrell and Kitching (188). Determination of conformational A-values (Table 14) showed that for this wide range of cyclohexylmercurials the axial conformer is preferred.

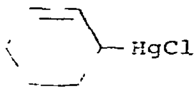
Full details have been provided concerning the ^{13}C NMR spectra of mercurated carbohydrate derivatives (189; cf. J. Organometal. Chem., 143 (1977) 284 for last year's Survey for data and discussion). The $^{199}Hg-^{1}H$ and $^{199}Hg-^{13}C$ couplings in the proton and ^{13}C NMR spectra of the series of methyl 2-deoxy-2- mercuri-D-pyranosides which were investigated served to delineate the angular dependence of ^{3}J and ^{4}J couplings. ^{13}C Chemical shifts, $^{199}Hg-^{13}C$ coupling constants, half-wave reduction potentials and ν(C=C) integral intensities have been discussed as evidence for σ-π conjugation in allylic mercurials (190). Such data were given for mercurials 95-100.

$CH_2=CHCH_2HgCl$

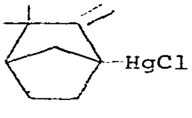
95



96



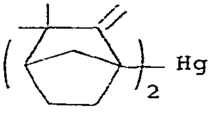
97



98

$(CH_2=CHCH_2)_2Hg$

99

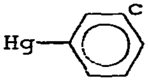


100

A linear dependence has been found of $^{1}J(^{199}Hg-^{13}C)$ and $^{2}J(^{1}H-C-^{199}Hg)$ for dibenzylmercury in various solvents, an observation which provides support for the idea that electronic factors are responsible for changes in spin-spin coupling constants on solvation of organomercurials (191). Other, more specialized NMR studies of methylmercury compounds have been reported (192, 193).

^{199}Hg NMR studies of cyclohexylmercurials have been carried out (188). Table 15 brings the observed chemical shift values.

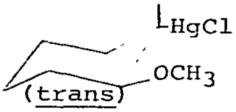
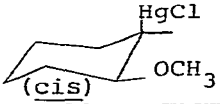
Table 14. Conformational A-Values for Mercury-Containing Groups in Cyclohexylmercurials, HgY, in CyclohexylHgY (188).

Group	Solvent	Temp. (°K)	K (ax/eq)	Measurement	A-Value[a]	
$HgOCOCH_3$[b]	CD_2Cl_2	193	1.84	C_1	-.235	
			1.70	$C_{2},6$	-.204	-.25±.06
			2.25	C_4	-.312	
$HgOCOCH_3$[b]	CD_2Cl_2/py $-d_5$	193	1.99	C_1	-.265	
			1.53	$C_{2,6}$	-.164	-.24±.08
			2.14	C_4	-.293	
HgCN[c]	CD_2Cl_2	193	1.38	C_1	-.124	
			1.40	$C_{2,6}$	-.129	
			1.50	C_4	-.156	-.14±.02
			1.54	CN	-.166	
HgCN[c]	CD_2Cl_2/py $-d_5$	193	1.58	C_1	-1.76	
			1.64	$C_{2,6}$	-.191	
			1.51	$C_{4,5}$	-.159	-.19±.04
			1.81	C_4	-.229	
	CD_2Cl_2/py $-d_5$	193	1.52	C_1	-.161	
			1.38	$C_{2,6}$	-.124	-.14±.03
			1.35	$C_{3,5}$	-.115	
			1.54	C_4	-.166	

For $(C_6H_{11})_2Hg$ (CD_2Cl_2:py $-d_5$) C_1 intensities indicate (a,a) is ∿40-45%; with (e,e) and (a,e) each about 25-30%.

a) $A = \Delta F^{o} = RT\ln K$ b) 22.62 MHz. c) 67.89MHz.

Table 15. ^{199}Hg Chemical Shifts of Cyclohexylmercurials (188).

Compound	Solvent	Temperature (°K)	Shift[a]
$C_6H_{11}HgOCOCH_3$	Toluene/pyridine	350	-618
		320	-614
		303	-610
	CH_2Cl_2/pyridine	303	-632
		245	-648(e) -556(a)
		215	-633(e) -556(a)
trans-4-CH_3-$C_6H_{10}HgOCOCH_3$	$CHCl_3$	303	-678(e)
$C_6H_{11}HgCN$	Toluene	350	-222
		320	-217
		303	-216
	CH_2Cl_2/pyridine	303	-209
		230	-249(e); -154(a)
		210	-240(e); -150(a)
$C_6H_{11}HgC_6H_5$	Toluene/pyridine	350	+105
		320	+109
	CH_2Cl_2/pyridine	303	+128
		230	+54(a); +172(a)
		210	+58(e); +172(a)
		200	+61(e); +173(a)
$(C_6H_{11})_2Hg$	CH_2Cl_2/pyridine	303	+252
		220[b]	+219(e?); +351(a?)
		210[b]	+222(e?); +349(a?)
 (trans)	$CHCl_3$	302	-386
 (cis)	$CHCl_3$	302	-365

a) Referenced to diphenylmercury in chloroform
b) a and e assignments not proven

INDOR methods were used to obtain the ^{199}Hg NMR spectrum of cyclopentadienylmethylmercury, $CH_3HgC_5H_5$ (194). Equal coupling to all five cyclopentadienyl protons was observed, which establishes that intramolecular exchange is responsible for the fluxional nature of this molecule.

D. Nuclear Quadrupole Resonance Spectroscopy

The ^{55}Mn and ^{35}Cl or ^{81}Br NQR spectra of manganocenylmercurials of type 101 (X = Cl, Br, $C_5H_4Mn(CO)_3$) have been measured (27).

101

E. Photoelectron Spectroscopy

The helium(I) photoelectron spectra of some dialkylmercury compounds have been reported (120). The ionization potentials, as defined in the equation below, are given in Table 16. It is

$$\text{R-Hg-R} \xrightarrow{I_D} \text{R-Hg-R}\cdot^{+} + e^{-}$$

apparent that increased chain-branching at the ß carbon atom does not markedly affect I_D, but that increased α-branching markedly lowers I_D.

Table 16. Effect of α- and ß-Branching on the Ionization Potentials of Dialkylmercury Compounds (120)[a]

α-Branching		ß-Branching	
R in R_2Hg	I.P.(eV)	R in R_2Hg	I.P.(eV)
Methyl	9.33	Ethyl	8.45
Ethyl	8.45	n-Propyl	8.29
i-Propyl	8.03	i-Butyl	8.30
t-Butyl	7.57	neo-Pentyl	8.30

a) First vertical ionization potentials by He(I) photoelectron spectroscopy.

F. Mass Spectroscopy

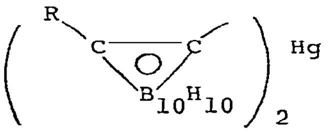
70 eV Mass spectra of dialkylmercury compounds (except for dimethylmercury) show mostly mercury-free fragments. On lowering the ionizing voltage to 20 and 15 eV., mercury-containing fragments become more important. Chemical ionization spectra serve better to give mercurial ions. When methane is the reagent gas, molecular ions, $R_2Hg\cdot^+$, are abundant, with lesser ions being $(R_2HgH - H_2)^+$, $(R_2HgH - RH)^+$ and $(R_2HgH - RCH_3)^+$. Using methane/water as the reagent gas, the oxomercurial cation $RHgOH_2^+$ becomes important. When isobutane is the reagent gas, the major ions observed are $R_2Hg\cdot^+$, $(R_2HgBu - RH)^+$, $(R_2HgBu - RCH_3)^+$ and $(R_2HgBu - RBu)^+$ (195).

A mass spectroscopic study of the photoionization of diphenylmercury has been reported (196).

11. PHYSICOCHEMICAL STUDIES OF ORGANOMERCURIALS

Dipole moment studies on compounds of type R_2Hg (R = Me, Et, Ph, CH_2=CH, PhC≡C) and RHgX (R = Ph, Me, Pr, Bu, C_7H_{15}, CH_2=CH; X = Cl, Br, I) (197) and cis- and trans-ClCH=CHHgX (X = Cl, Br, I) (198) have been reported.

A polarographic study of the specific solvation (in CH_3CN, DMSO, DMF, HMPA and tetramethylurea) of carboranylmercurials of type 102, of $(PhC{\equiv}C)_2Hg$ and of $PhHgCCl_3$ has been carried out (199). It was found that the better the donor properties of the solvent, the more difficult was the electrochemical reduction of the mercurial. The carboranylmercurials could not be reduced at all in the presence of 2,2'-bipyridine. Such effects were not seen with dibenzylmercury and thus seem to be confined to the more Lewis acidic R_2Hg compounds.



(R = Ph, Me)

102

CNDO-MO calculations have been carried out on methylmercuric halides (200).

12. ANALYTICAL ASPECTS OF ORGANOMERCURY CHEMISTRY

Among the studies devoted to the analysis of organomercurials were the following:

- Nanogram TLC analysis of phenylmercury compounds (201).
- Mechanism of reaction GC of phenylmercury compounds (202).
- GC analysis of organomercurials (15).
- GC determination of inorganic and organomercury compounds in biological samples (203).
- Liquid-liquid distribution of CH_3HgX and PhHgX (X = Cl, Br, I) between 0.1M HCl (and 3M HCl) and fourteen different organic solvents using ^{203}Hg-tagged mercurials (204).
- Removal of elemental mercury and mercury compounds from gases and solutions (review) (205).
- Analytical applications of o-hydroxymercuribenzoic acid (206).
- Determination of mercury and $CH_3Hg(II)$ in fish (207).
- Microassay of mercury in organic substances (208).

REFERENCES

1. C. A. McAuliffe, ed., "The Chemistry of Mercury", Macmillan of Canada/Maclean-Hunter Press, Toronto, 1977, viii + 288 pp ($ 34.95).
2. D. Seyferth, Science, 200 (1978) 678.
3. S. I. Ioffe, L. M. Leonteva and V. A. Tartakovskii, Usp. Khim., 46 (1977) 1658.
4. O. M. Nefedov, A. I. D'yachenko and A. K. Prokof'ev, Usp. Khim., 46 (1977) 1787; Russ. Chem. Rev., 46 (1977) 941.
5. G. G. Furin, O. I. Andreevskaya and G. G. Yakobson, Zh. Org. Khim., 12 (1976) 2627.
6. S. B. Awad, D. S. Brown, S. C. Cohen, R. E. Humphries and A. G. Massey, J. Organometal. Chem., 127 (1977) 127.
7. D. Seyferth, G. J. Murphy and R. A. Woodruff, J. Organometal. Chem., 141 (1977) 71.
8. M A. Zanakova, O. G. Smirnova, I. G. Trostyanskaya and I. F. Lutsenko, Zh. Obshch. Khim., 46 (1976) 2471.
9. T. Chivers and R. Ram, Can. J. Chem., 55 (1977) 2554.
10. F. Glockling, N. S. Hosmane, V. B. Mahale, J. J. Swindall, L. Magos and T. J. King, J. Chem. Res. (S) (1977) 116; (M) (1977) 1201.

11. V. I. Sokolov, G. Z. Suleimanov, V. V. Bashilov, T. Kh. Kurbanov, I. A. Amirslanov and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 1894.
12. V. I. Sokolov, L. L. Troitskaya and O. A. Reutov, J. Organometal. Chem., 133 (1977) C28.
13. L. C. Costa and G. M. Whitesides, J. Am. Chem. Soc., 99 (1977) 2390.
14. B. M. Mikhailov, M. E. Gurskii and M. G. Gverdtsiteli, Izv. Akad. Nauk SSSR, Ser. Khim. (1976) 2402.
15. V. Luckow and H. A. Rüssel, J. Chromatog., 138 (1977) 381.
16. M. G. Voronkov, N. F. Chernov and T. A. Dekina, Dokl. Akad. Nauk SSSR, 230 (1976) 853.
17. E. M. Panov, O. P. Syutkina, V. I. Lodochnikova and K. A. Kocheshkov, Zh. Obshch. Khim., 47 (1977) 838.
18. A. Roy and A. K. Ghosh, Inorg. Chim. Acta, 24 (1977) L89.
19. M. H. Abraham, D. F. Dadjour and M. R. Sedaghat-Herati, J. Chem. Soc., Perkin Trans. II (1977) 1225.
20. L. J. Dizikes and A. Wojcicki, J. Am. Chem. Soc., 99 (1977) 5295.
21. J. H. Espenson and T.-H. Chao, Inorg. Chem., 16 (1977) 2553.
22. V. C. W. Chu and D. W. Gruenwedel, Bioinorg. Chem., 7 (1977) 169.
23. G. B. Deacon, G. J. Farquharson and J. M. Miller, Austral. J. Chem., 30 (1977) 1013.
24. Yu. A. Ol'dekop, N. A. Maier, A. A. Erdman and V. P. Prokopovich, Zh. Obshch. Khim., 47 (1977) 1673.
25. Yu. A. Ol'dekop, N. A. Maier, A. A. Erdman, T. A. Rubakha and I. A. Shingel', Dokl. Akad. Nauk SSSR, 235 (1977) 828.
26. N. D. Kagramanov, A. K. Mal'tsev and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 1335.
27. A. N. Nesmeyanov, V. V. Korol'kov, E. V. Bryukhova, S. I. Kuznetsov, T. P. Tolstaya and G. K. Semin, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 1899.
28. L. C. Costa, G. B. Young and G. M. Whitesides, J. Organometal. Chem., 134 (1977) 151.
29. Yu. A. Ol'dekop, N. A. Maier and V. L. Shirokii, Dokl. Akad. Nauk SSR, 229 (1976) 637.
30. G. M. McNamee, B. C. Willett, D. M. La Perriere and D. G. Peters, J. Am. Chem. Soc., 99 (1977) 1831.
31. L. A. Avaca, E. R. Gonzalez and N. R. Stradiotto, Electrochim. Acta, 22 (1977) 225.

32. K. Hayashi, S. Kawai, T. Ohno and Y. Maki, J. Chem. Soc., Chem. Comm., (1977) 158.

33. M. Akagi, Y. Fujita and E. Takabatake, Photochem. Photobiol., 26 (1977) 363.

34. M. Steinbach and G. Wegner, Makromol. Chem., 178 (1977) 1671.

35. H. Schmidbaur, O. Gasser, T. E. Fraser and E. A. V. Ebsworth, J. Chem. Soc., Chem. Comm. (1977) 334.

36. G. B. Deacon, W. D. Raverty and D. G. Vince, J. Organometal. Chem., 135 (1977) 103.

37. S. W. Schmalz and D. T. Haworth, J. Inorg. Nucl. Chem., 39 (1977) 1715.

38. M. G. Voronkov, N. F. Chernov and A. A. Tatarinova, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 1839.

39. F. Glockling and J. J. Sweeney, J. Chem. Res. (S) (1977) 35; (M) (1977) 615.

40. J. A. Morrison, L. L. Gerchman, R. Eujen and R. J. Lagow, J. Fluorine Chem., 10 (1977) 333.

41. T. E. Bitterwolf and A. C. Ling, Syn. React. Inorg. Metal-Org. Chem., 7 (1977) 367.

42. G. N. Bockerman and R. W. Parry, J. Inorg. Nucl. Chem., H. H. Hyman Memorial Vol., (1976) 55.

43. A. L. Rheingold and P. Choudhury, J. Organometal. Chem., 128 (1977) 155.

44. I. D. Sakekov, A. A. Maksimenko and L. L. Ladatko, Zh. Obshch. Khim., 47 (1977) 2229.

45. P. W. J. de Graaf, A. J. De Koning, J. Boersma and G. J. M. Van der Kerk, J. Organometal. Chem., 141 (1977) 345.

46. O. A. Reutov, V. I. Sokolov, G. Z. Suleimanov, V. V. Bashilov and I. A. Amiraslanov, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 2147.

47. A. Segnitz, E. Kelly, S. H. Taylor and P. M. Maitlis, J. Organometal. Chem., 124 (1977) 113.

48. A. Z. Rubezhov, A. S. Ivanov and S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim. (1976) 2348.

49. G. B. Deacon and G. J, Farquharson, Austral. J. Chem., 30 (1977) 293.

50. G. B. Deacon and G. J. Farquharson, Austral. J. Chem., 30 (1977) 1701.

51. A. N. Nesmeyanov, I. N. Lisichkina, A. N. Vanchikov and T. P. Tolstaya, Uzb. Akad. Nauk SSSR, Ser. Khim. (1977) 1204.

52. B. Giese and J. Meister, Chem. Ber., 110 (1977) 2588.

53. B. Giese and J. Meixner, Tetrahedron Lett. (1977) 2779.

54. B. Giese and J. Meixner, Tetrahedron Lett. (1977) 2783.

55. B. Giese, Angew. Chem., 88 (1976) 159.

56. B. Giese and J. Meister, Angew. Chem., 89 (1977) 178.

57. G. A. Razuvaev, Yu. D. Semchikov, S. F. Zhil'tsov, V. A. Sokolova and L. M. Mazanova, Dokl. Akad. Nauk SSSR, 231 (1976) 353.

58. R. C. Larock and J. C. Bernhardt, J. Org. Chem., 42 (1977) 1680.

59. K. Tanaga, N. Hayama, T. Okamoto, Y. Sakakibara and S. Oka, Bull. Chem. Soc. Japan, 50 (1977) 2741.

60. A. Kasahara, T. Izumi and A. Suzuki, Bull. Chem. Soc. Japan, 50 (1977) 1639.

61. S. M. Brailovskii, G. A. Kabalina, V. S. Shestakova and O. N. Temkin, Zh. Org. Khim., 13 (1977) 1158.

62. I. Rhee, M. Ryang, T. Watanabe, H. Omura, S. Murai and N. Sonoda, Synthesis (1977) 776.

63. R. A. Amos and J. A. Katzenellenbogen, J. Org. Chem., 42 (1977) 2537.

64. J. Barluenga and A. M. Mastral, Anal. Quim., 73 (1977) 1032.

65. W. Ried and S.-W. Park, J. prakt. Chem., 319 (1977) 1011.

66. R. N. Butler and A. B. Hanahoe, J. Chem. Soc., Chem. Comm. (1977) 622.

67. P. J. Chenier, J. Org. Chem., 42 (1977) 2643.

68. M. E. Jason and J. A. Ibers, J. Am. Chem. Soc., 99 (1977) 6012.

69. E. Yoshii, T. Koizumi, E. Kitatsuji, T. Kawazoe and T. Kaneko, Heterocycles, 4 (1976) 1663.

70. N. Shimizu, T. Fujioka, S. Ishizuka, T. Tsuji and S. Nishida, J. Am. Chem. Soc., 99 (1977) 5972.

71. R. F. Cunico and H. M. Lee, J. Am. Chem. Soc., 99 (1977) 7613.

72. V. S. Aksenov and G. A. Terent'eva, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 623.

73. S. A. Cerefice and E. K. Fields, U.S. patent 4,005,122 (1977); Chem. Abstr., 87 (1977) 39020c.

74. M. Weidenbruch, H. Pesel, W. Peter and R. Steichen, J. Organometal. Chem., 141 (1977) 9.

75. M Weidenbruch and C. Pierrard, Chem. Ber., 110 (1977) 1545.

76. W. Kimpenhaus and J. Buddrus, Chem. Ber., 110 (1977) 1305

77. D. Tevault, D. P. Strommen and K. Nakamoto, J. Am. Chem. Soc., 99 (1977) 2997.

78. I. C. Ambidge, S. K. Dwight, C. M. Rynard and T. T. Tidwell, Can. J. Chem., 55 (1977) 3086.

79. L. N. Balyatinskaya, Zh. Obshch. Khim., 47 (1977) 198.

80. D. Jasserand, J. P. Girard, J. C. Rossi and R. Granger, Tetrahedron, 32 (1976) 1535.

81. T. M. Cheung, D. Horton and W. Weckerle, Carbohydrate Res., 59 (1977) 276.

82. R. Baker, D. A. Evans and P. G. McDowell, J. Chem. Soc., Chem. Comm. (1977) 111.

83. G. Ortar and I. Torrini, Tetrahedron, 33 (1977) 859.

84. A. I. Dyadchencko, A. V. Semenovskii and V. A. Smit, Izv. Akad. Nauk SSSR, Ser. Khim. (1976) 2281.

85. N. A. Keiko, T. N. Musorina, I. D. Kalikhman, E. I. Brodskaya, A. A. Tatarinova, B. Kh. Kopylovskaya and M. G. Voronkov, Zh. Obshch. Khim., 47 (1977) 421.

86. R. Meyer, L. Gorrichon and P. Maroni, J. Organometal. Chem., 129 (1977) C7.

87. M. G. Voronkov, N. F. Chernov and I. D. Kalikhman, Dokl. Akad. Nauk SSSR, 233 (1977) 361.

88. B. F. G. Johnson, J. Lewis, D. G. Parker and S. R. Postle, J. Chem. Soc., Dalton Trans. (1977) 794.

89. L. J. Dizikes and A. Wojcicki, J. Organometal. Chem., 137 (1977) 79.

90. S. V. Krivun, S. V. Sayapina and S. N. Baranov, USSR patent 541,848 (1977); Chem. Abstr., 87 (1977) 6205p.

91. A. J. Bloodworth and M. E. Loveitt, J. Chem. Soc., Perkin Trans. I (1977) 1031.

92. M. Barrelle and M. Apparu, Tetrahedron, 33 (1977) 1309.

93. R. J. Spear and W. A. Jensen, Tetrahedron Lett. (1977) 4535.

94. D. Szemenyei, D. Steichen and J. E. Byrd, J. Mol. Catal., 2 (1977) 105.

95. Yu. S. Shabarov, S. G. Bandaev and L. D. Sychkova, Vestn. Mosk. Univ., Khim., 17 (1976) 726; Chem. Abstr., 87 (1977) 5279d.

96. Yu. S. Shabarov, S. G. Bandaev and L. D. Sychkova, Vestn. Mosk. Univ., Khim., 17 (1976) 620; Chem. Abstr., 86 (1977) 121029a.

97. S. S. Mochalov, T. S. Oretskaya, V. V. Karpova and Yu. S. Shabarov, Zh. Org. Khim., 13 (1977) 836.
98. V. I. Boev and A. V. Dombrovskii, Zh. Obshch. Khim., 47 (1977) 727.
99. N. F. Chernov, T. A. Dekina and M. G. Voronkov, Zh. Obshch. Khim., 47 (1977) 794.
100. L. N. Balyatinskaya and T. V. Kurchenko, Zh. Obshch. Khim., 47 (1977) 436.
101. S. R. Singh, J. Indian Chem. Soc., 53 (1976) 595; Chem. Abstr., 86 (1977) 29921n.
102. N. Mullick and R. K. Nanda, J. Indian Chem. Soc., 54 (1977) 1018.
103. G. A. Razuvaev, N. S. Vasileiskaya, E. P. Oleinik, N. N. Vavilina and D. V. Muslin, Zh. Obshch. Khim., 46 (1976) 2720.
104. L. M. Stock and T. L. Wright, J. Org. Chem., 42 (1977) 2875.
105. Z. Yashida, H. Konishi, Y. Kamitori and H. Ogoshi, Chem. Lett. (1977) 1341.
106. H. Schmidbaur and W. Richter, Z. anorg. allg. Chem., 429 (1977) 222.
107. E. Glozbach and J. Lorberth, J. Organometal. Chem., 132 (1977) 359.
108. P. Krommes and J. Lorberth, J. Organometal. Chem., 127 (1977) 19.
109. R. Grüning and J. Lorberth, J. Organometal. Chem., 129 (1977) 55.
110. C. Glidewell, J. Organometal. Chem., 136 (1977) 7.
111. K. P. Butin, A. N. Ryabtsev and O. A. Reutov, Dokl. Akad. Nauk SSSR, 233 (1977) 1102.
112. K. P. Butin, V. N. Shishkin, I. P. Beletskaya and O. A. Reutov, Zh. Org. Khim., 13 (1977) 2024.
113. K. P. Butin, V. N. Shishkin, I. P. Beletskaya and O. A. Reutov, Dokl. Akad. Nauk SSSR, 231 (1976) 100.
114. I. P. Beletskaya, V. N. Shishkin, K. P. Butin and O. A. Reutov, Zh. Org. Khim., 13 (1977) 2241.
115. M. H. Abraham, P. L. Grellier and M. J. Hogarth, J. Chem. Soc., Perkin Trans. II (1977) 221.
116. S. E. Ibrahim and M. M. Kreevoy, J. Phys. Chem., 81 (1977) 2143.
117. C. C. Lee and R. Reichle, J. Org. Chem., 42 (1977) 2058.

118. W. A. Nugent and J. K. Kochi, J. Organometal. Chem., 124 (1977) 327.

119. W. A. Nugent and J. K. Kochi, J. Organometal. Chem., 124 (1977) 349.

120. W. A. Nugent and J. K. Kochi, J. Organometal. Chem., 124 (1977) 371.

121. I. P. Beletskaya, G. A. Armankina and A. K. Pikaev, Izv. Akad. Nauk, SSSR, Ser. Khim. (1976) 2403.

122. T. S. Oretskaya, Yu. S. Shabarov, S. S. Mochalov and V. V. Karpova, Zh. Org. Khim., 13 (1977) 2124.

123. G. A. Razuvaev, E. N. Gladshev, V. N. Latyaeva, E. V. Krasil'nikova, A. N. Lineva and Yu. N. Novotorov, Dokl. Akad. Nauk, 231 (1976) 1138.

124. E. Yu. Belyaev and S. V. Petrova, Zh. Org. Khim., 13 (1977) 1220.

125. T. Iwayanagi, M. Matsuo and Y. Saito, J. Organometal. Chem 135 (1977) 1.

126. I. I. Giuashvili, L. A. Katsman and M. N. Vargaftik, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 80.

127. I. I. Giuashvili, M. N. Vargaftik, R. R. Dogonadze and L. A. Katsman, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 1433.

128. F. J. C. Rossotti and R. J. Whewell, J. Chem. Soc., Dalton Trans. (1977) 1223.

129. F. J. C. Rossotti and R. J. Whewell, J. Chem. Soc., Dalton Trans. (1977) 1229.

130. R. J. Maguire, S. Anand, H. Chew and W. D. Adams, J. Inorg. Nucl. Chem., 38 (1976) 1659.

131. A. J. Canty and R. Kishimoto, Inorg. Chim. Acta, 24 (1977) 109.

132. R. L. Coates and M. M. Jones, J. Inorg. Nucl. Chem., 39 (1977) 677.

133. A. J. Canty and R. K. Tyson, Inorg. Chim. Acta, 24 (1977) L77.

134. D. N. Kravtsov, A. S. Peregudov and E. M. Rokhlina, J. Organometal. Chem., 128 (1977) C27.

135. A. J. Canty and R. Kushimcto, Austral. J. Chem., 30 (1977) 669.

136. G. Pouskouleli, P. Kourounakis and T. Theophanides, Inorg. Chim. Acta, 24 (1977) 45.

137. S.-W. Park and W. Ried, Justus Liebigs Ann. Chem. (1977) 106.

138. G. C. Stocco, Inorg. Chim. Acta, 24 (1977) L65.

139. D. Breitinger and W. Morell, Z. Naturforsch., 32b (1977) 1022.

140. J. Liesk and G. Klar, Z. anorg. allg. Chem., 435 (1977) 103.

141. U. Behrens, K. Hoffmann and G. Klar, Chem. Ber., 110 (1977) 3672.

142. C. A. Evans, D. L. Rabenstein, G. Geier and I. W. Erni, J. Am. Chem. Soc., 99 (1977) 8106.

143. F. Glockling and V. B. Mahale, Inorg. Chim. Acta, 25 (1977) L117.

144. L. I. Belousova, O. A. Kruglaya, V. V. Neretivi, I. D. Kalikhman, N. A. Ivanova, A. A. Tatarinova and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 2070.

145. R. W. Chrisman, S. Mansy, H. J. Peresie, A. Ranade, T. A. Berg and R. S. Tobias, Bioinorg. Chem., 7 (1977) 245.

146. V. I. Bregadze, V. Ts. Kampel' and N. N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 1630; J. Organometal. Chem., 136 (1977) 281.

147. L. I. Zakharkin and I. V. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 1885.

148. V. Ts. Kampel', K. P. Butin, V. I. Bregadze and N. N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 1454.

149. H. Müller and L. Rösch, J. Organometal. Chem., 133 (1977) 1.

150. A. R. Clagett, W. H. Ilsley, T. J. Anderson, M. D. Glick and J. P. Oliver, J. Am. Chem. Soc., 99 (1977) 1797.

151. L. Rösch, Angew. Chem., 89 (1977) 257.

152. L. Rösch, Angew. Chem., 89 (1977) 497.

153. G. A. Razuvaev, L. N. Bochkarev, G. S. Kalinina and M. N. Bochkarev, Inorg. Chim. Acta, 24 (1977) L40.

154. G. Avar and W. P. Neumann, J. Organometal. Chem., 131 (1977) 207.

155. H. U. Buschhans, M. Lehnig and W. P. Neumann, J. Chem. Soc., Chem. Comm. (1977) 129.

156. D. V. Gendin, O. A. Kruglaya, T. I. Vakul'skaya, L. P. Petukhov and N. S. Vyazankin, Zh. Obshch. Khim., 47 (1977) 1427.

157. G. A. Razuvaev, E. N. Gladyshev, P. Ya. Bayushkin, G. A. Abakumov and E. S. Klimov, Izv. Akad. Nauk SSSR, Ser. Khim. (1976) 2762.

158. O. A. Kruglaya, I. B. Fedot'eva, B. V. Fedot'ev, I. D. Kalikhman, E. I. Brodskaya and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1976) 1887.

159. O. A. Kruglaya, I. B. Fedot'eva, B. V. Fedot'ev, I. D. Kalikhman, E. I. Brodskaya and N. S. Vyazankin, J. Organometal. Chem., 142 (1977) 155.

160. O. A. Kruglaya, B. A. Gostevskii and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 250.

161. M. N. Bochkarev, G. A. Razuvaev, L. P. Maiorova, N. P. Makarenko, V. I. Sokolov, V. V. Bashilov and O. A. Reutov, J. Organometal. Chem., 131 (1977) 399.

162. D. P. Graddon and J. Mondal, J. Organometal. Chem., 132 (1977) 1.

163. M. Cano Esquivel, A. Santos Macias and I. Ballester Reventos, J. Inorg. Nucl. Chem., 39 (1977) 1153.

164. G. Geier, I. Erni and R. Steiner, Helv. Chim. Acta, 60 (1977) 9.

165. N. T. Berberova, D. N. Sadzhaya and O. Yu. Oklobystin, Dokl. Akad. Nauk SSSR, 229 (1976) 92.

166. Yu. V. Kolodyazhnyi, T. Ya. Mel'nikova, A. K. Prokof'ev and O. A. Osipov, Zh. Obshch. Khim., 46 (1976) 1830.

167. M. Kh. Minacheva and E. M. Brainina, Izv. Akad. Nauk SSSR, Ser. Khim. (1976) 2621.

168. D. Grdenić, B. Kamenar and A. Nagl, Acta Cryst. B, 33 (1977) 587.

169. D. J. Brauer, H. Bürger and R. Eujen, J. Organometal. Chem., 135 (1977) 281.

170. R. A. Smith, M. Torres and O. P. Strausz, Can. J. Chem., 55 (1977) 3527.

171. R. A. Smith, M. Torres and O. P. Strausz, Can. J. Chem., 55 (1977) 2752.

172. L. G. Kuz'mina, N. G. Bokii, Yu. T. Struchkov, V. I. Minkin, L. P. Olekhnovich and I. E. Mikhailov, Zh. Strukt. Khim., 18 (1977) 122.

173. Y.-S. Wong, A. J. Carty and P. C. Chieh, J. Chem. Soc., Dalton Trans. (1977) 1157.

174. Y.-S. Wong, A. J. Carty and P. C. Chieh, J. Chem. Soc., Dalton Trans. (1977) 1801.

175. H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, J. Chem. Soc., Chem. Comm. (1977) 737.

176. I. S. Butler and M. L. Newbury, Spectrochim. Acta A, 33 (1977) 669.

177. C. G. Barraclough, G. E. Berkovic and G. B. Deacon, Austral. J. Chem., 30 (1977) 1905.
178. K. Volka, P. Adamek, I. Stibor and Z. Ksandr, Spectrochim. Acta A, 33 (1977) 241.
179. K. Sone, M. Aritaki, K. Hiraoka and Y. Fukuda, Bull. Chem. Soc. Japan, 49 (1976) 2015.
180. G. A. Razuvaev, V. A. Kuznetsov, A. N. Egorochkin, A. A. Klimov, A. N. Artemov and N. I. Sirotkin, J. Organometal. Chem., 128 (1977) 213.
181. P. L. Yadav, N. K. Jha and V. Ramkrishna, Bull. Chem. Soc. Japan, 50 (1977) 2594.
182. G. A. Domrachev and V. T. Bychkov, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 237.
183. T. Iwayanagi, T. Ibusuki and Y. Saito, J. Organometal. Chem., 128 (1977) 145.
184. M. J. Albright, J. N. St. Denis and J. P. Oliver, J. Organometal. Chem., 125 (1977) 1.
185. R. Grüning, P. Krommes and J. Lorberth, J. Organometal. Chem., 128 (1977) 167.
186. P. F. Barron, D. Doddrell and W. Kitching, J. Organometal. Chem., 132 (1977) 351.
187. H. Müller, L. Rösch, W. Erb and R. Zeisberg, J. Organometal. Chem., 140 (1977) C17.
188. P. F. Barron, D. Dodrell and W. Kitching, J. Organometal. Chem., 139 (1977) 361.
189. V. G. Gibb and L. D. Hall, Carbohydrate Res., 55 (1977) 239.
190. A. N. Nesmeyanov, V. A. Blinova, L. I. Denisovich, Z. S. Klemenkova, P. V. Petrovskii, I. V. Shchirina-Eingorn, E. I. Fedin, V. T. Aleksanyan and I. I. Kritskaya, Dokl. Akad. Nauk SSSR, 235 (1977) 362.
191. V. S. Petrosyan and J. D. Roberts, Org. Magn. Reson., 9 (1977) 555.
192. A. J. Brown, O. W. Howarth, P. Moore and A. D. Bain, J. Magn. Reson., 28 (1977) 317.
193. C. R. Lassigne and E. J. Wells, Can. J. Chem., 55 (1977) 1303.
194. R. J. Goodfellow and S. R. Stobart, J. Magn. Reson., 27 (1977) 143.
195. L. Simonotti and C. Trombini, Inorg. Chim. Acta, 21 (1977) L27.

196. Yu. L. Sergeev, M. E. Akopyan and F. I. Vilesov, Teor. Eksp. Khim., 13 (1977) 129; Chem. Abstr., 87 (1977) 5195y.

197. T. Ya. Mel'nikova, Yu. V. Kolodyazhnyi, A. K. Prokof'ev and O. A. Osipov, Zh. Obshch. Khim., 46 (1976) 1820.

198. Yu. V. Kolodyazhnyi, T. Ya. Mel'nikova, O. Yu. Okhlobystin, O. A. Osipov and A. K. Prokof'ev, Zh. Obshch. Khim., 46 (1976) 1816.

199. N. T. Berberova and O. Yu. Okhlobystin, Zh. Obshch. Khim., 47 (1977) 726.

200. S. Sakaki, N. Hagiwara, N. Iwasaki and A. Ohyoshi, Bull. Chem. Soc. Japan, 50 (1977) 14.

201. V. Luckow and H. A. Rüssel, Chromatographia, 9 (1976) 578.

202. V. Luckow and H. A. Rüssel, J. Chromatog., 138 (1977) 381.

203. C. J. Cappon and J. C. Smith, Anal. Chem., 49 (1977) 365.

204. J. Starý and K. Kratzer, Radiochem. Radioanal. Lett., 28 (1977) 53.

205. K.-H. Bergk, F. Wolf and S. Eckert, Z. Chem., 17 (1977) 85.

206. M. Wronski, Talanta, 24 (1977) 347.

207. --, The Analyst, 102 (1977) 769.

208. A. Campiglio, Mikrochim. Acta, 2 (1977) 71.