MERCURY

ANNUAL SURVEY COVERING THE YEAR 1979

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TABLE OF CONTENTS

1. REVIEWS

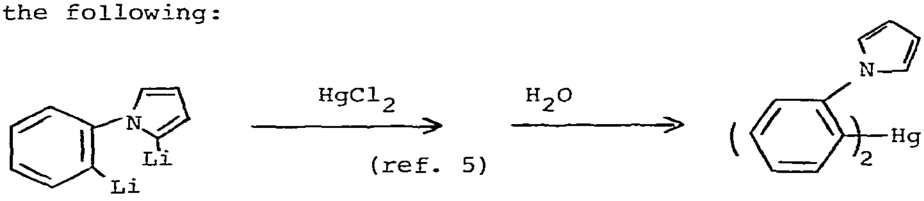
Reviews covering the following topics in organomercury chemistry have appeared:

- Organomercurial applications in organic synthesis (1);
- Silicon-containing organomercury compounds (2);
- Reactions of Pd(0) and Pt(0) complexes with organomercurials (3);
- Synthesis and reactions of allylic mercury compounds (4)

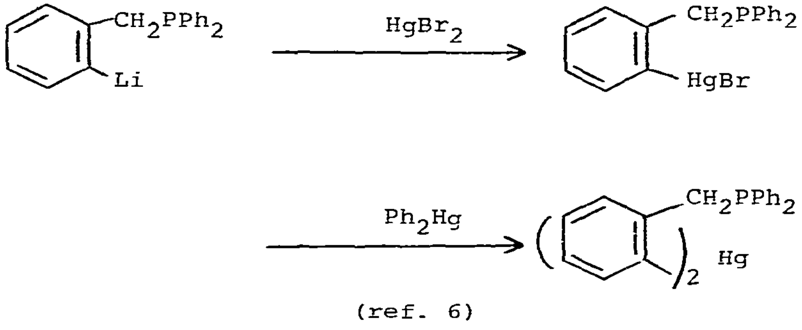
2. PREPARATION OF ORGANOMERCURY COMPOUNDS

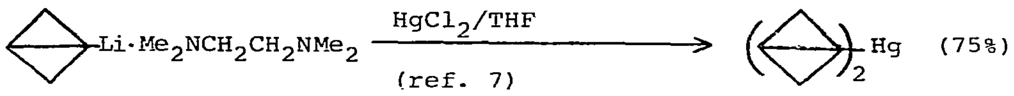
A. Organometallic Routes

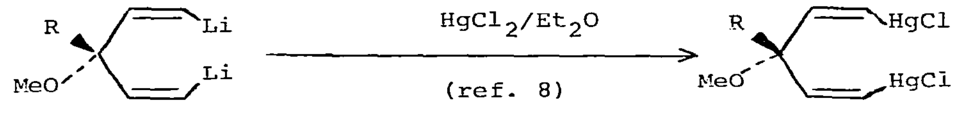
Organomercurials are prepared routinely by the organolithium and Grignard routes. Novel preparations reported in 1979 include the following:



(The lithium on the pyrrole ring did not react and was removed on hydrolysis.)



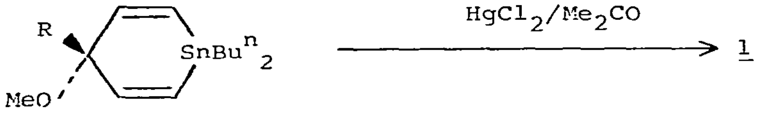




(R = cyclo-C_6H_{11})

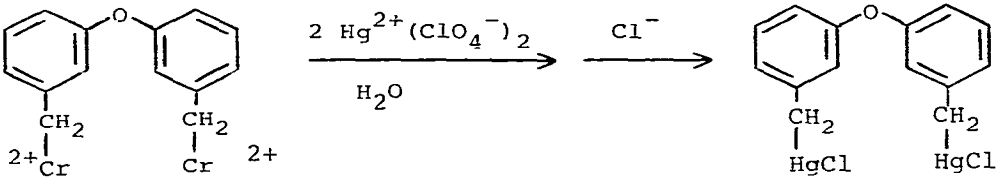
1

Compound 1 also was prepared by the organotin route (8):



The compound with R = Ph also was prepared in this manner.

Transfer of organic substituents from transition metals to mercury has received further study, more from the point of view of kinetics and mechanism of the transfer process. Espenson, who has been an active contributor to this area, has studied the kinetics of some mercury-for-chromium substitutions (9):



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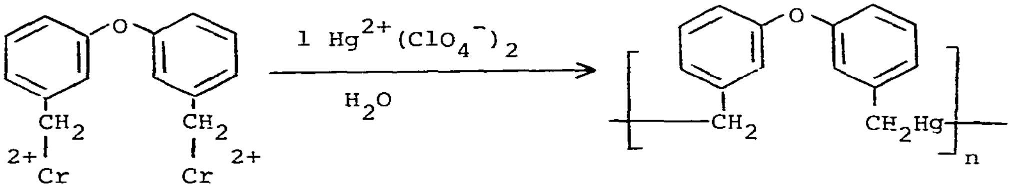
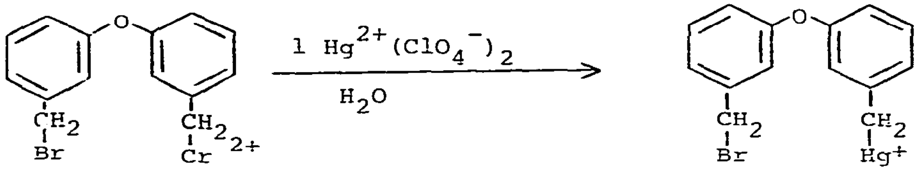




The kinetics of the reaction of 2 with an excess of Hg^{2+} were measured using stopped-flow techniques: $k_{obs} = 4.74 \times 10^4$ $dm^3 mol^{-1} s^{-1}$ at 25°C ($[H^+] = 0.500\underline{M}$; $\mu = 0.500\underline{M}$).

The alkyl group cleavage from an organoiron and an organotungsten complex by mercuric chloride was found to proceed with retention of configuration at carbon, while such cleavage of an alkylmanganese complex proceeded with inversion (10).

Retention

$\underline{threo}$-$PhCHDCHDFe(CO)_2Cp + HgCl_2 \longrightarrow CpFe(CO)_2Cl + PhCHDCHDHgCl$

$\underline{trans}$-$\underline{threo}$-$PhCHDCHDW(CO)_2(PEt_3)Cp + HgCl_2 \longrightarrow PhCHDCHDHgCl$

$+$ $\underline{cis}$-$CpW(CO)_2(PEt_3)Cl$

Inversion

$\underline{cis}$-$\underline{threo}$-$PhCHDCHDMn(CO)_4PEt_3 + HgCl_2 \longrightarrow PhCHDCHDHgCl$

$+$ $\underline{cis}$-$Mn(CO)_4(PEt_3)Cl$

The stereochemistry of the PhCHDCHDHgCl products was determined by proton NMR studies and by cleavage with bromine in pyridine, a reaction known to occur with retention of configuration.

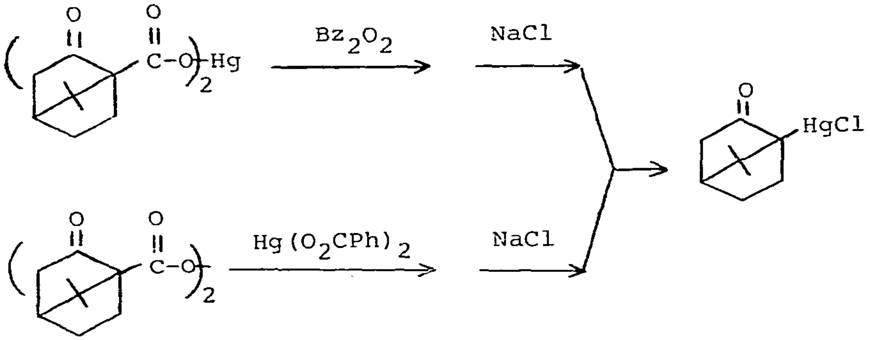
B. Radical Processes

Ol'dekop and Maier and their coworkers have continued their studies of the radical-induced decarboxylation of mercury(II) carboxylates,

$$Hg(O_2CR)_2 \xrightarrow{h\nu \text{ or peroxide}} RHgO_2CR + CO_2,$$

with an investigation of the decarboxylation of the Hg(II) salts of o-carborane-9(12)-, m-carborane-9(10)-, o-carborane-1-, and m-carborane-1-carboxylic acids (11). The first two are weak acids and, as expected, they decarboxylated smoothly under radical conditions to give the respective carboranylmercuric salt. Thermal decarboxylation of the Hg(II) salt of m-carborane-9(10)-carboxylic acid at 210-240°C and of its 1,10-phenanthroline complex at 155°C gave metallic mercury rather than organomercury products. On the other hand, the thermal decarboxylation of the Lewis base (1,10-phen, bipy) adducts of the Hg(II) salt of the strong o-carborane-1-carboxylic acid proceeded readily, giving $R_2Hg \cdot nL$ type products in high yield. m-Carborane-1-carboxylic acid is of intermediate acidity. Thermolysis of its Hg(II) salt and of the 1,10-phenanthroline adduct of the latter resulted in decarboxylation, but only very low yields of di-*m*-carboranylmercury were formed.

We take this occasion to correct an unfortunate error in the 1977 mercury Annual Survey (p. 145). The radical decarboxylations shown in the equations below actually take place without



racemization; the radical intermediate is configurationally stable (12).

The electrochemical generation of organic radicals at a mercury cathode is a well-known process for Hg-C bond formation. Di-*n*-decylmercury is formed in the reduction of *n*-decyl iodide at mercury electrodes in DMF (0.1*F* $Me_4N^+ClO_4^-$) at potentials positive with respect to the polarographic maximum. The mechanism of the *n*-decyl iodide reduction has received detailed study (13). It is dependent on potential, electrolysis time and the concentration of water present in the system. Decyl radicals form di-*n*-decylmercury *via*:

$$R\cdot\text{(adsorbed)} + Hg \longrightarrow RHg\cdot\text{(adsorbed)}$$

$$2\ RHg\cdot\text{(adsorbed)} \longrightarrow R_2Hg + Hg$$

Decyl carbanions, on the other hand, react with DMF and water to give other products.

The cocondensation (at -196°C) of mercury vapor with radicals which have been generated by C-C bond homolysis in a radiofrequency glow discharge from hexafluoroethane and ethane provides another route to organomercury compounds. Prepared in this way have been $(CF_3)_2Hg$ in high yield (89%) and $(CH_3)_2Hg$ in low yield (9%) (14), but these syntheses are not competitive with the more usual laboratory procedures.

$$X_3C\text{-}CX_3 \xrightarrow[\text{glow discharge}]{\text{radio frequency}} 2X_3C\cdot \xrightarrow{Hg} (CX_3)_2Hg\quad (X = F,\ H)$$

C. Miscellaneous

Bis[bis(trimethylsilyl)amino]mercury, $[(Me_3Si)_2N]_2Hg$, has been shown to be an effective reagent for the direct mercuration, under mild conditions, of very weakly acidic organic compounds, e.g. (15):

$$PhC{\equiv}CH \quad (pK_a\ 28.8) \longrightarrow (PhC{\equiv}C)_2Hg$$

$$CH_3C(O)CH_3 \quad (pK_a\ 26.5) \longrightarrow (CH_3C(O)CH_2)_2Hg$$

$$PhC(O)CH_3 \quad (pK_a\ 24.7) \longrightarrow (PhC(O)CH_2)_2Hg$$

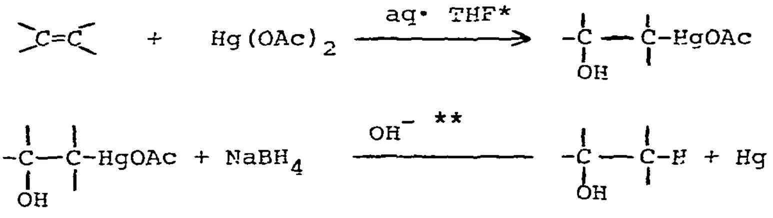
$$PhCH_2CN \quad (pK_a\ 22.2) \longrightarrow (Ph\underset{|}{C}HCN)_2Hg$$

Acetonitrile (pK_a 31.3) and $Me_3CC(O)CH_3$ were not mercurated under these conditions.

3. MERCURATION OF UNSATURATED COMPOUNDS

A. Olefins and Polyenes

The solvomercuration of olefins provides a general and very useful route to organofunctional organomercurials, and the solvomercuration-demercuration sequence has found much application in organic synthesis in recent years. Especially the oxymercuration-demercuration sequence is often used:



$$>C{=}C< \ + \ Hg(OAc)_2 \xrightarrow{aq.\ THF^{*}} -\underset{OH}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}-HgOAc$$

$$-\underset{OH}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}-HgOAc + NaBH_4 \xrightarrow{OH^{-}\ **} -\underset{OH}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{|}{C}}-H + Hg$$

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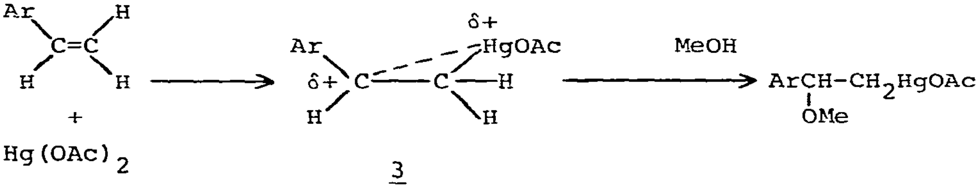
* henceforth $\xrightarrow{Hg(OAc)_2/THF} \ = \ \xrightarrow{OM}$ oxymercuration

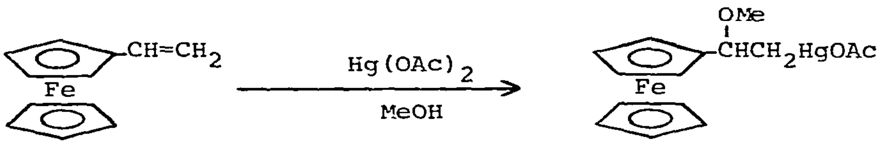
** henceforth $\xrightarrow{NaBH_4/OH^{-}} \ = \ \xrightarrow{DM}$ demercuration

A number of papers in 1979 were devoted to the study and utilization of these and related reactions.

Much work has been devoted to the mechanism of the oxymercuration reaction, especially to the question of the intermediacy of charged species and their structure. Lewis and Azoro (16) have found that the logarithms of the rates of the methoxymercuration of p-substituted styrenes correlate excellently both with σ and σ^+. The rho values obtained, $\rho = -3.16 \pm 0.09$; $\rho^+ = -2.76 \pm 0.11$, were rationalized in terms of an unsymmetrical bridged ion of type 3. The observed pseudo-first order rates, in methanol at 25°C, were (Z in $p\text{-}ZC_6H_4CH{=}CH_2$, $k_{obs} \times 10^4$ in sec^{-1}): CH_3, 3280 ± 61; H, 665 ± 19; F, 584 ± 17; Br, 162 ± 5; CN, 5.93 ± 0.33; NO_2, 3.42 ± 0.07. *



The results obtained in the methoxymercuration of a number of alkylvinylferrocenes depended on the number, location and nature of the alkyl groups, with both vinyl addition and cyclopentadienyl ring mercuration being observed (17):



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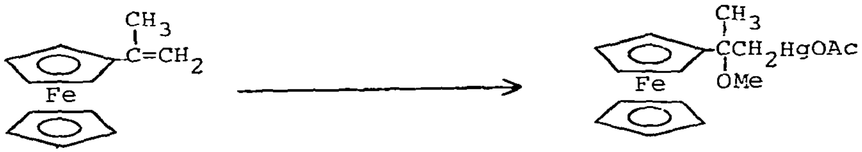
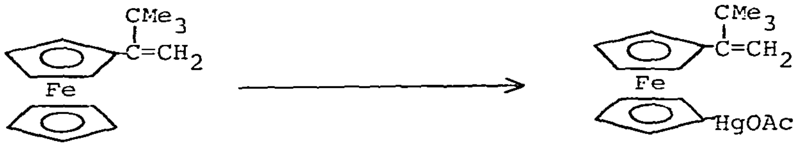
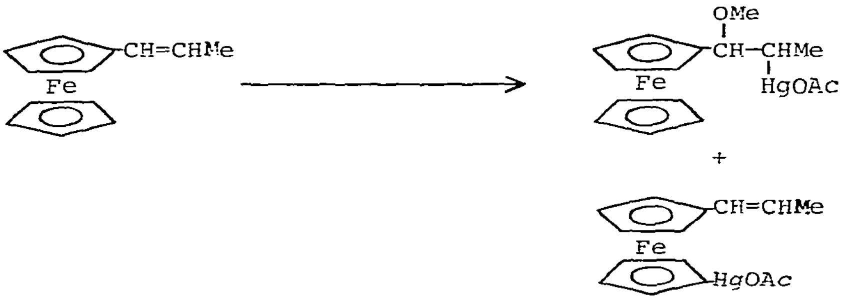
[*] Note the previous study of the relative rates of methoxymercuration of nine substituted styrenes in which a somewhat better correlation of log k(rel) against σ than against σ^+ was observed, with $\rho = -2.25 \pm 0.15$: G. Müller-Hagen and W. Pritzkow, J. prakt. Chem., 311(1969) 874.







This difference in behavior observed for the five vinylic ferrocenes was interpreted in terms of both polar and steric effects. The kinetics of these reactions were studied. The observed rates are shown in Table 1. The relatively small difference between the methoxymercuration rates of styrene and vinylferrocene was explained in terms of a positively charged intermediate which has little carbonium ion character, i.e., a symmetrical mercurinium ion.

Brown and his coworkers (18) have carried out a detailed investigation of the regio- and stereochemistry of the oxymercuration-demercuration of alkyl-substituted cyclohexenes and cyclopentenes. The equations below give their results.

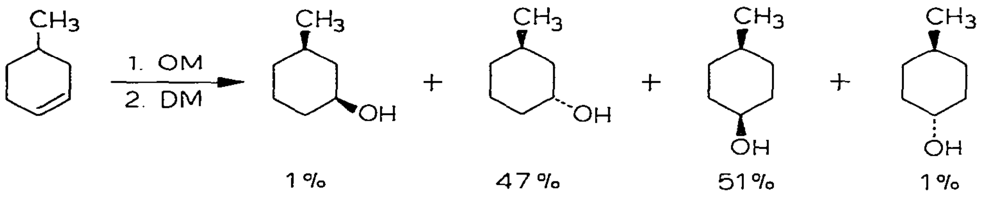
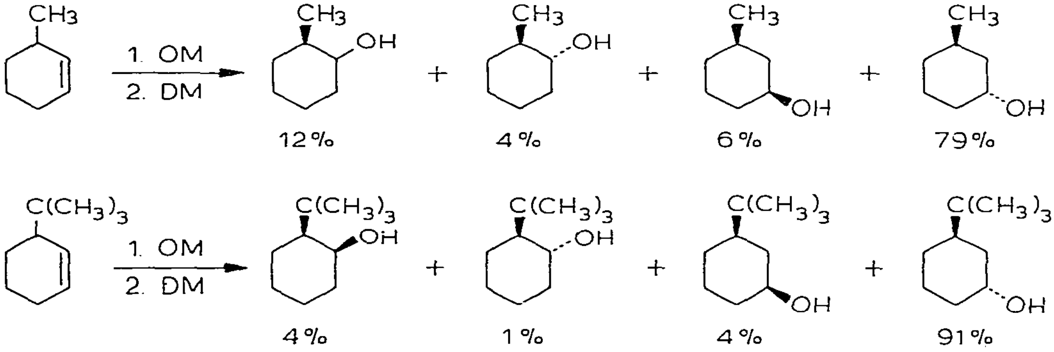


TABLE 1

SECOND ORDER RATE CONSTANTS FOR THE REACTION OF MERCURIC ACETATE WITH VINYLFERROCENES AND STYRENE IN METHANOL, AT 25°C

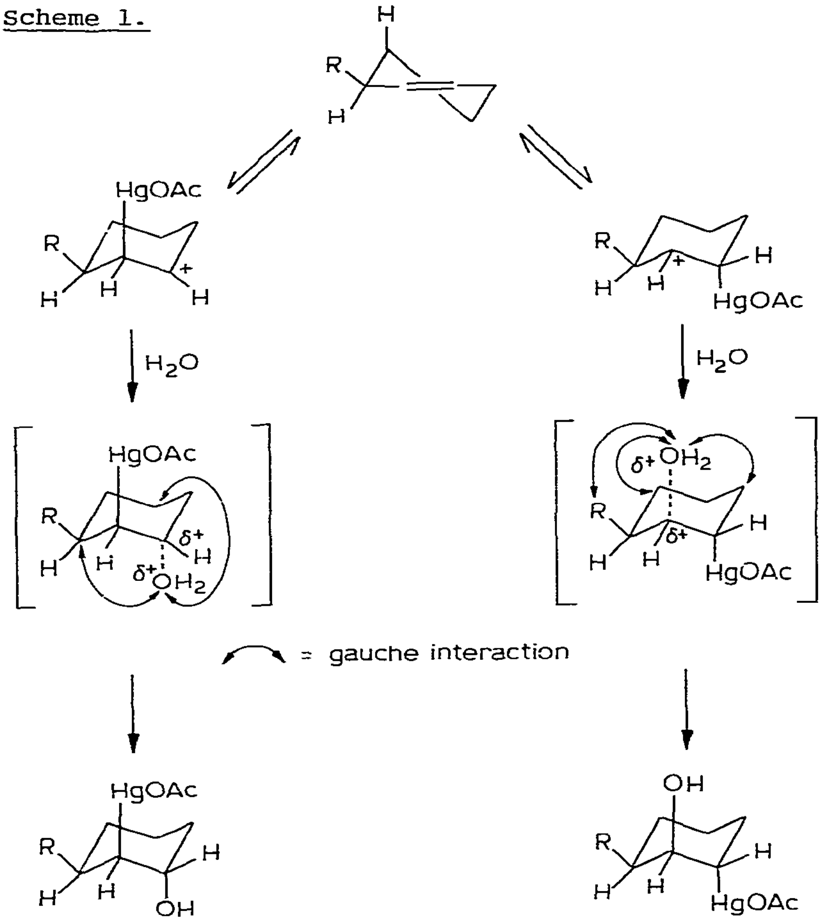
Compound	$k_{addition}$ (M^{-1} s^{-1})	$k_{substitution}$ (M^{-1} s^{-1})
$Fc-CH=CH_2$	230 ±30	
$Fc-C(CH_3)=CH_2$	910 ±80	
$Fc-C(t-Bu)=CH_2$		0.24 ± 0.02
$Fc-CH=CH-CH_3$	0.67± 0.04	0.37 ± 0.02
$Fc-CH=C(CH_3)_2$		0.26 ± 0.02
$Ph-CH=CH_2$	10.4 ± 0.5	
FcH		0.25 ± 0.02

In contrast to the lack of significant steric effect in the above reaction, such effects become important when the alkyl substituent is closer to the C=C bond:

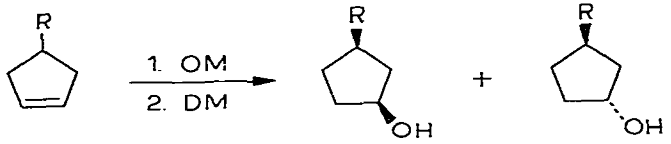


The product regio- and stereoselectivity result from the difference in nonbonded interactions encountered when the water nucleophile attacks the positively charged intermediate as shown in Scheme 1.

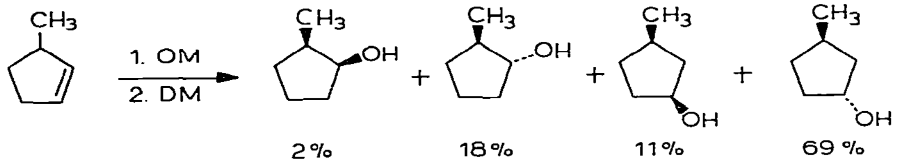
Scheme 1.

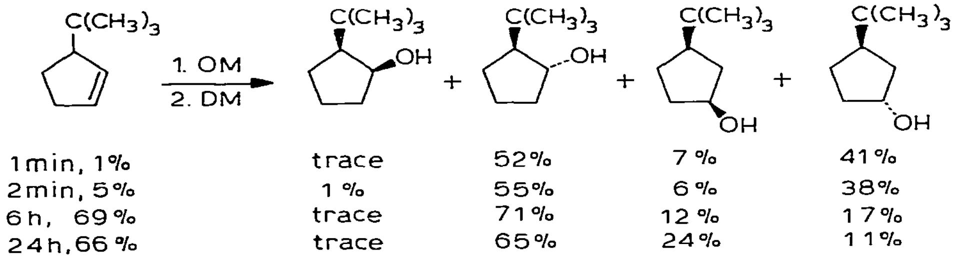


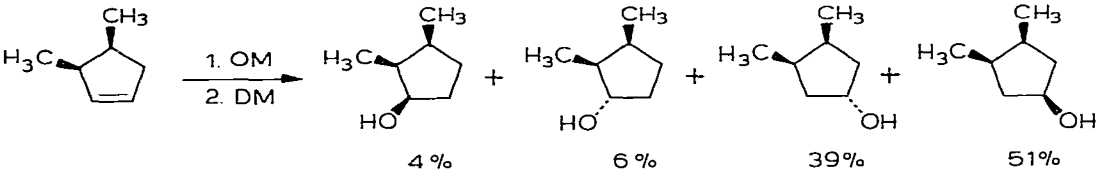
In the case of cyclopentenes the regio- and stereochemistry of product formation is not readily predictable because the C_5 ring is flexible.

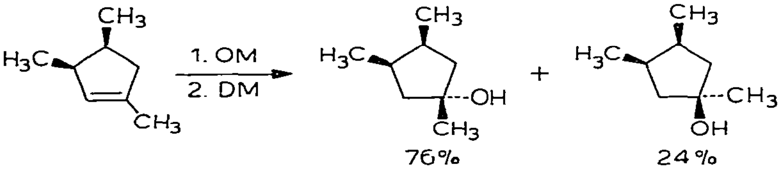


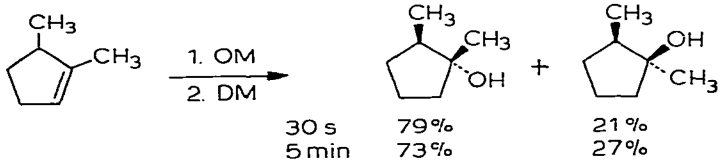
R = CH_3	77%	23%
R = $C(CH_3)_3$	88%	12%



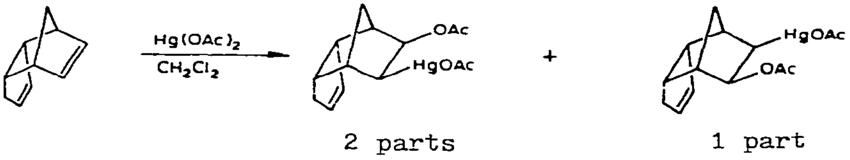


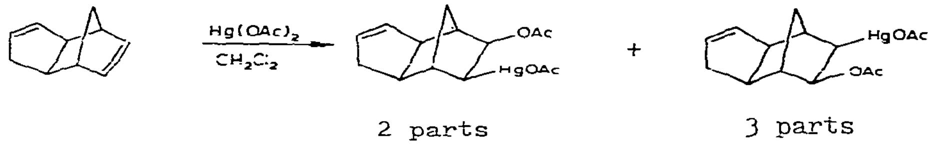


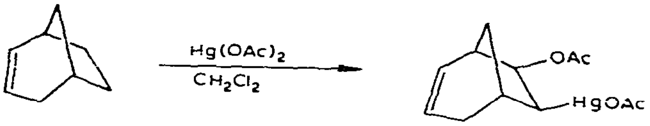




Acetoxymercuration reactions of endo- and exo-dicyclopentadiene and bicyclo[3.2.1]octa-2,6-diene have been reported by Japanese workers (19). The structures of the adducts were determined using ^{13}C NMR spectroscopy and chemical shifts and J(^{13}C-^{199}Hg) values of the products are tabulated in this paper.

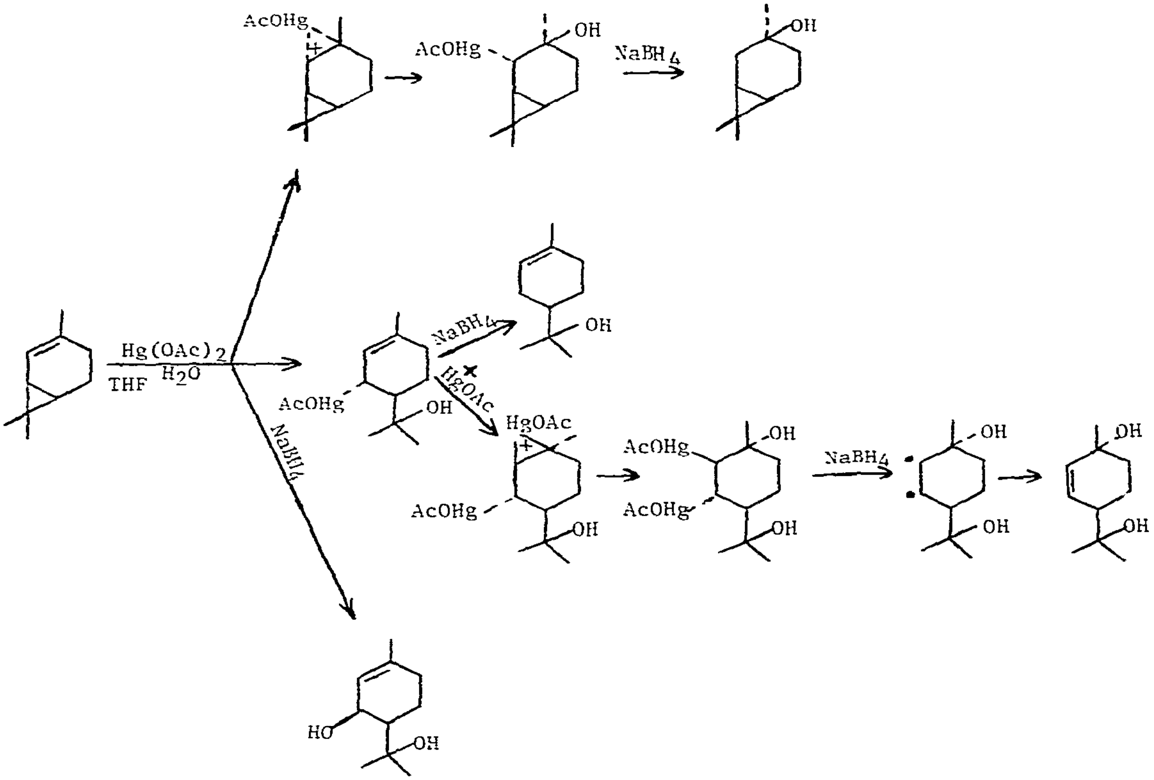




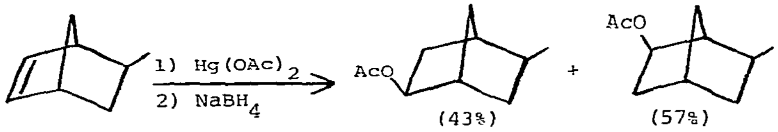


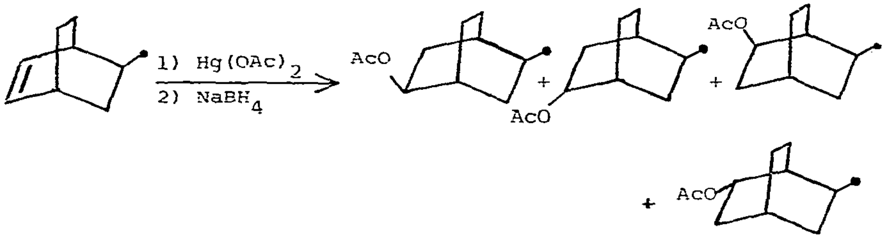
Russian workers have examined the oxymercuration of bicyclic olefins:

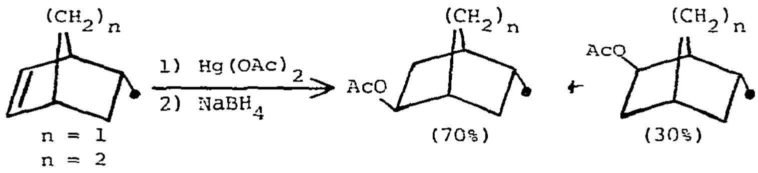
2-Carene (20). The oxymercuration of this compound proceeds both at the C=C bond and at the cyclopropane ring to give mono- and bis-adducts:

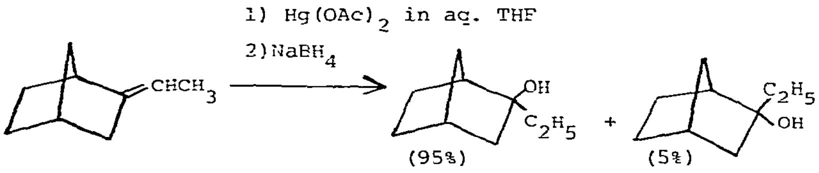


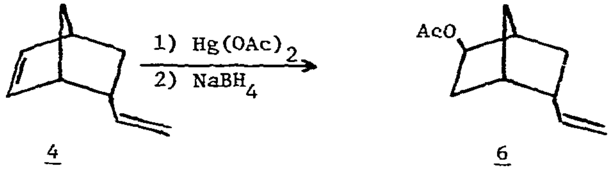
Substituted bicylo[2.2.1]hept-2-enes and bicyclo [2.2.2]oct-2-enes (21):

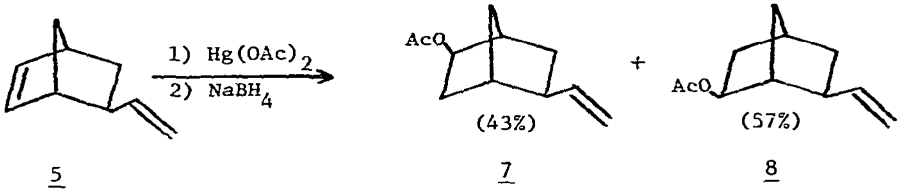




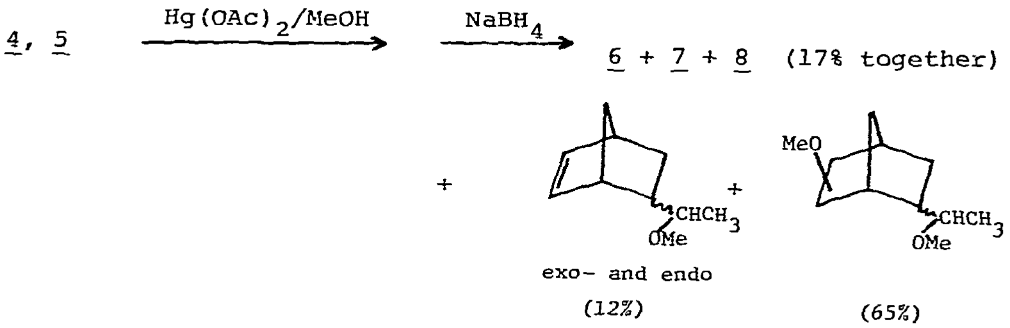




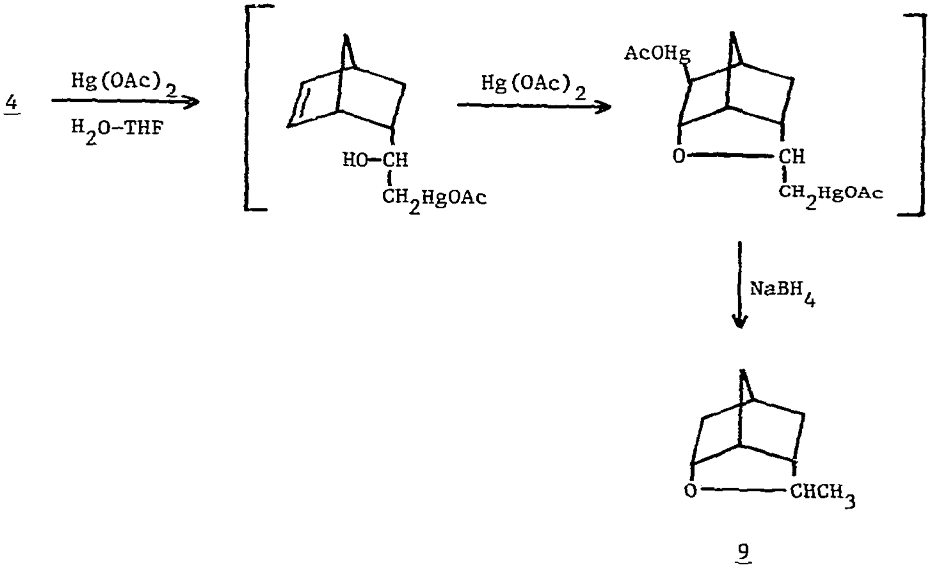




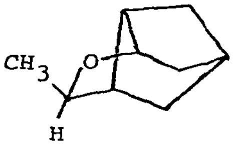
However, in methanol:



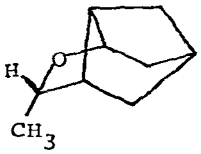
and in water:



^{13}C NMR studies showed 9 to be a 60:40 mixture of 9a and 9b.

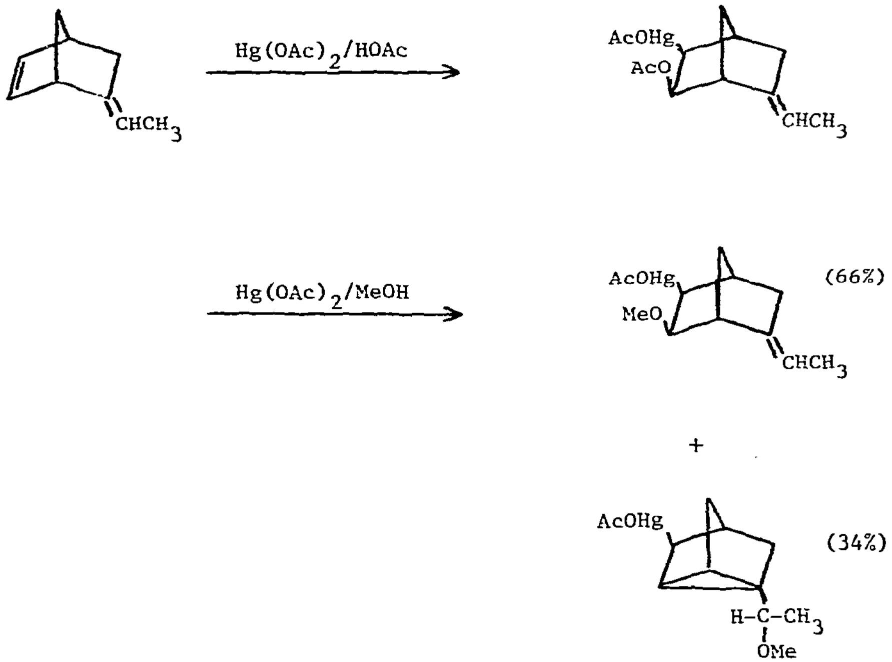


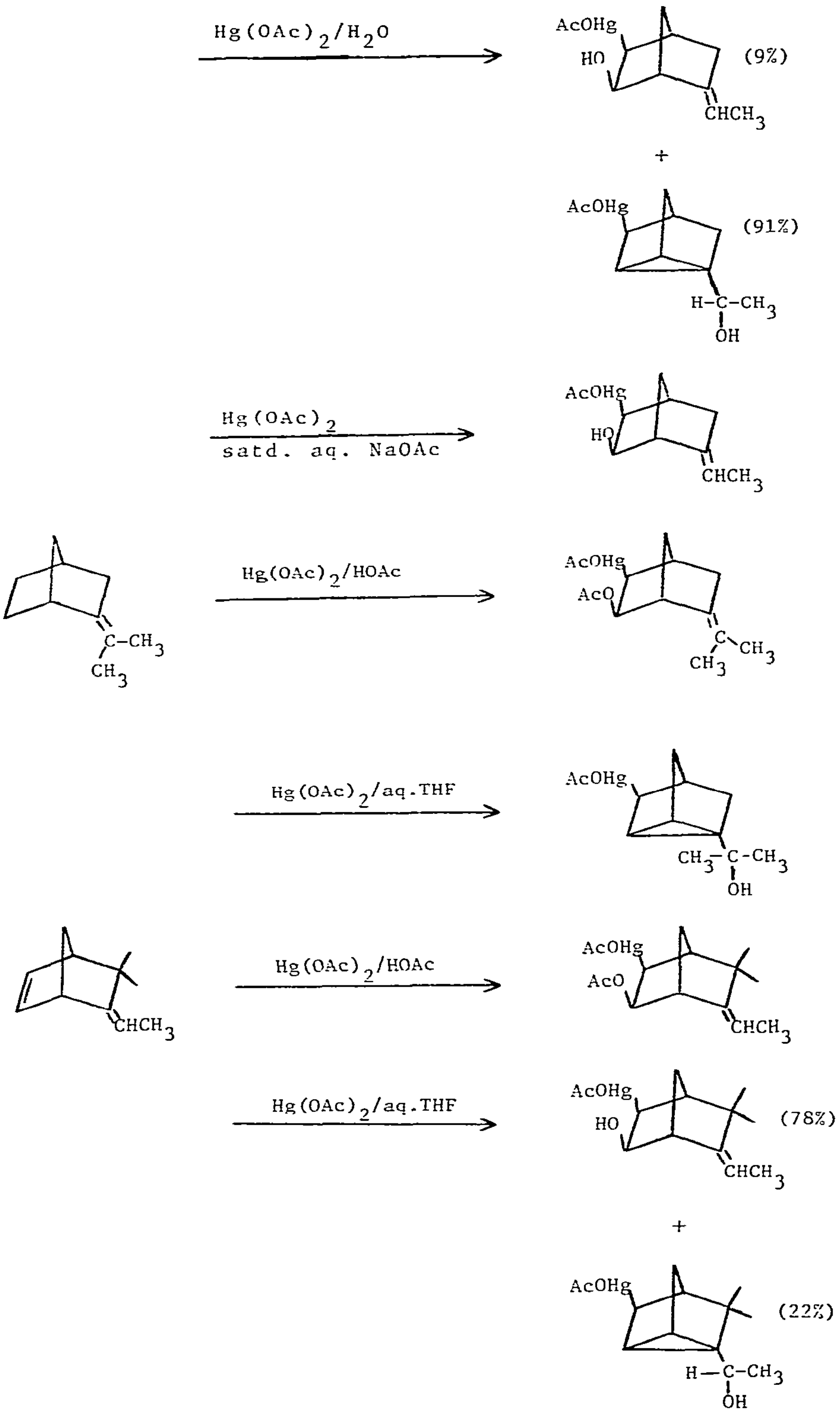
9a



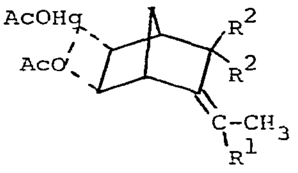
9b

Substituted 5-ethylidenebicyclo[2.2.1]hept-2-enes (22). Two types of products were observed, depending on the reaction medium, as shown in the equations below.

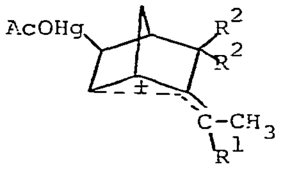



Hg(OAc)$_2$/H$_2$O
AcOHg
HO
CHCH$_3$
(9%)
+
AcOHg
H–C–CH$_3$
OH
(91%)
Hg(OAc)$_2$
satd. aq. NaOAc
AcOHg
HO
CHCH$_3$
C–CH$_3$
CH$_3$
Hg(OAc)$_2$/HOAc
AcOHg
AcO
C–CH$_3$
CH$_3$
Hg(OAc)$_2$/aq.THF
AcOHg
CH$_3$–C–CH$_3$
OH
CHCH$_3$
Hg(OAc)$_2$/HOAc
AcOHg
AcO
CHCH$_3$
Hg(OAc)$_2$/aq.THF
AcOHg
HO
CHCH$_3$
(78%)
+
AcOHg
H—C–CH$_3$
OH
(22%)

It was reasoned that in solvents of low dielectric constant (THF, HOAc) HgOAc$^+$OAc$^-$ ion pairs add via a four-centered transition state to the less substituted norbornene C=C bond, as in 10. However, in water, methanol and aqueous THF, HgOAc$^+$ (solvent-separated) adds to form the charged intermediate 11 which may undergo nucleophilic attack at the ethylidene carbon atom. It is noteworthy that when the dissociation of Hg(OAc)$_2$ is suppressed by using aqueous saturated sodium acetate as the reaction medium instead of water, addition occurs according to 10. Also studied was the NaBH$_4$ -demercuration of these solvomercuration products.

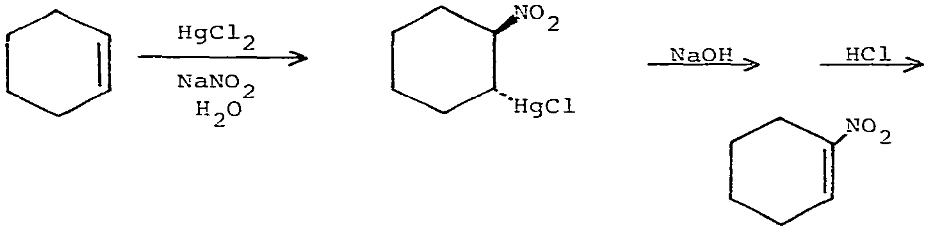


10



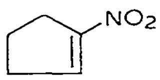
11

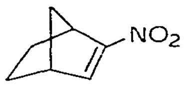
Nitro-olefins, which can be reagents of some utility, have been prepared by Corey and Estreicher (23a) by the known olefin nitromercuration reaction:

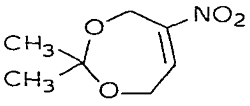


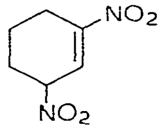
(80%)

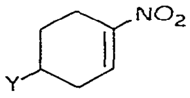
Also prepared by this procedure were the vinylic nitro compounds shown below.

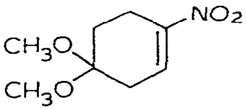


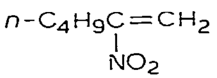




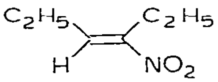








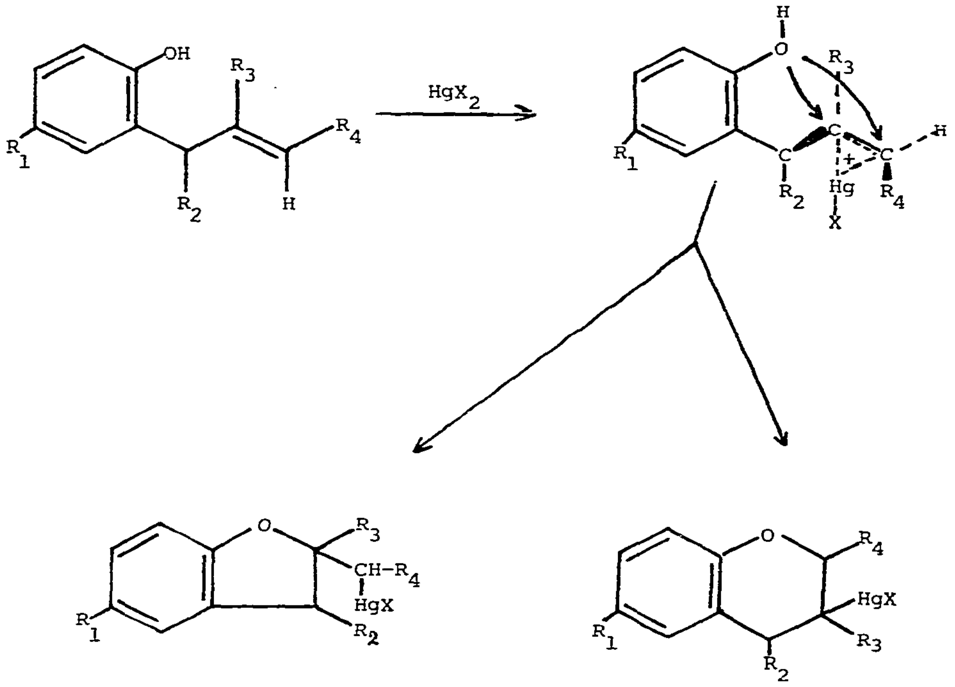
$n\text{-}C_4H_9\underset{\displaystyle NO_2}{\underset{|}{C}}=CH_2$



Y = COOCH3   Y = CN

Of particular utility in organic synthesis is the intramolecular oxymercuration-demercuration reaction which gives cyclic products. New examples of such reactions have been reported.

ortho-Allylphenols have been mercurated using mercuric acetate in aqueous THF or mercuric chloride in water, followed by reduction of the cyclic mercurial thus produced with alkaline $NaBH_4$ (23). The formation of a five- or a six-membered ring is possible, e.g.:



The results of these mercuration experiments are shown in Table 2. In each case, the mercurial was reduced with $NaBH_4$ to convert the CH_2HgX substituent to CH_3.

TABLE 2. Mercuration of o-Allylphenols (23)

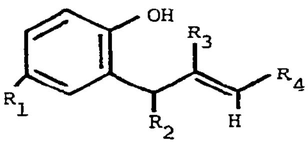
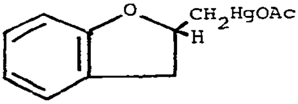
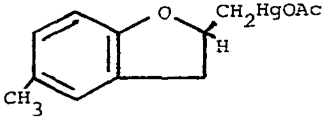
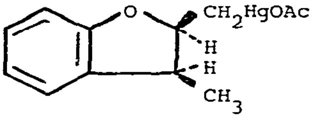
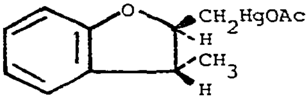
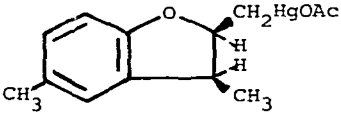
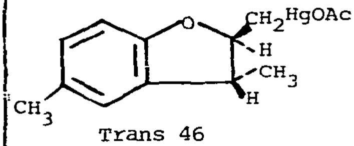
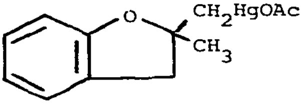
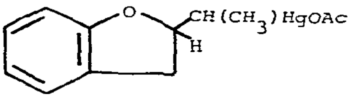
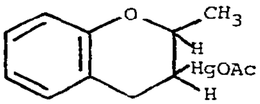
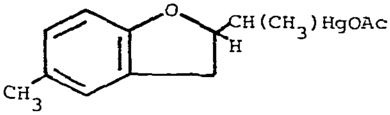
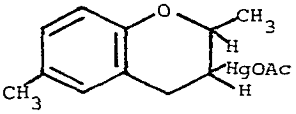
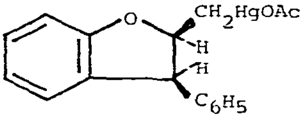
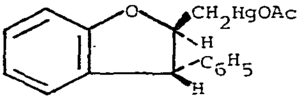
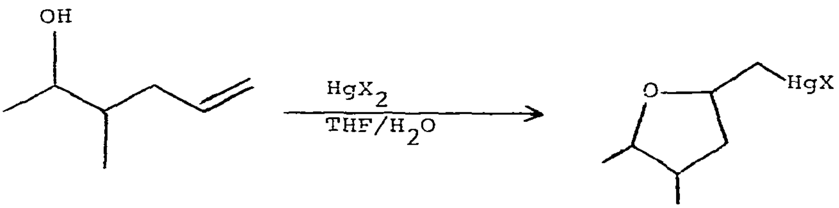
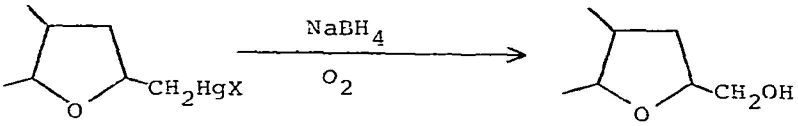
Allylphenol	Products		
	Benzofuran derivative	(%)	Benzopyran derivative (%)
$R_1 = R_2 = R_3 = R_4 = H$		100	———
$R_1 = CH_3; R_2 = R_3 = R_4 = H$		100	———
$R_1 = R_3 = R_4 = H;$ $R_2 = CH_3$	 Cis 56  Trans 44	100	———
$R_1 = R_2 = CH_3;$ $R_3 = R_4 = H$	 Cis 54  Trans 46	100	———
$R_1 = R_2 = R_4 = H;$ $R_3 = CH_3$		100	———

TABLE 2

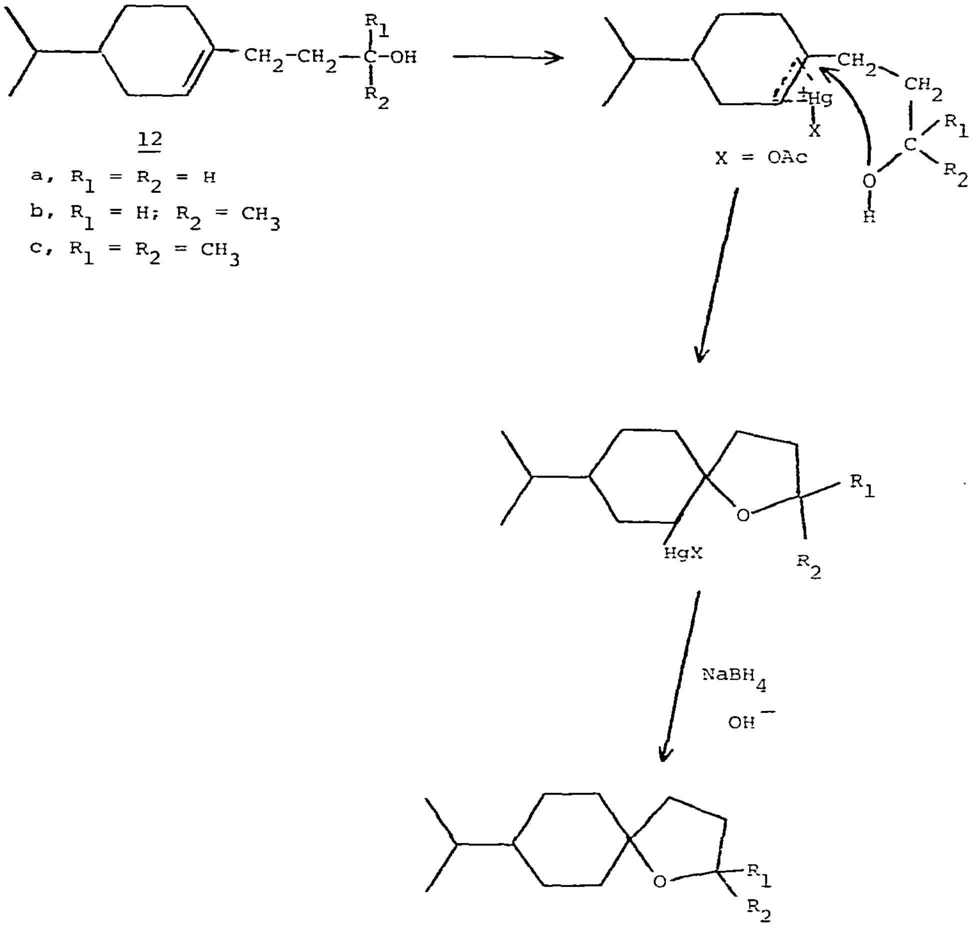
$R_1 = R_2 = R_1 = H$; $R_4 = CH_3$	 52	 48
$R_1 = R_4 = CH_3$; $R_2 = R_3 = H$	 51	 49
$R_1 = R_3 = R_4 = H$; $R_2 = C_6H_5$	 Cis 45  Trans 55 100	———

Similar reactions have been carried out in which the organomercury products were oxidized to the corresponding alcohols using NaBH$_4$/O$_2$ (24). Table 3 shows the mercurated tetrahydrofurans thus produced and the alcohols derived from them.





Spiro derivatives of tetrahydrofuran also were prepared by this procedure from unsaturated alcohols of type 12 (25):



12

a, $R_1 = R_2 = H$

b, $R_1 = H$; $R_2 = CH_3$

c, $R_1 = R_2 = CH_3$

A mixture of cis and trans isomers resulted in the ring closure process, e.g., 13a and 13b, in 32:68 proportion in the case of 12a.

TABLE 3. Alcohols from Cyclized Mercuration Products of Unsaturated Alcohols (24).

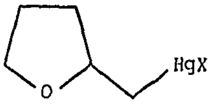
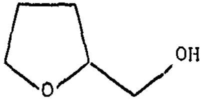
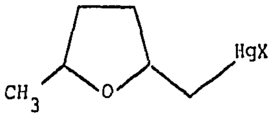
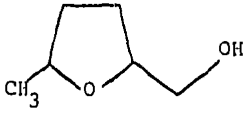
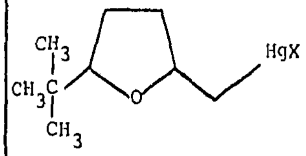
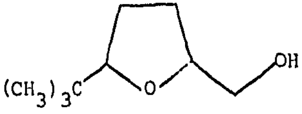
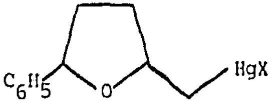
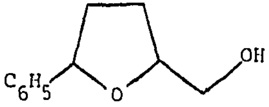
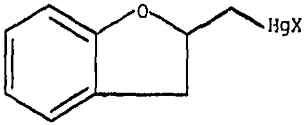
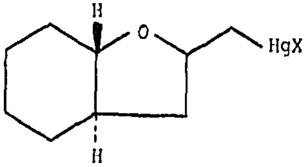
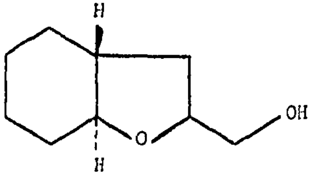
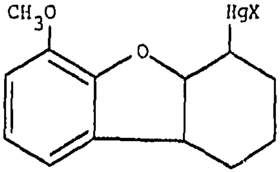
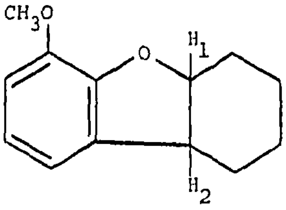
Mercurial			Alcohol		
	X=OAc	X=Cl			
	70	90^+			10
	65	90^+			20
		75			40
		60			25

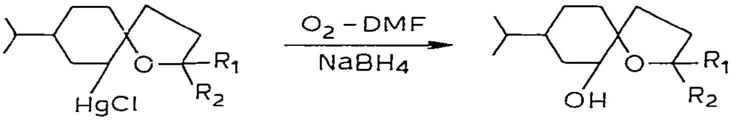
TABLE 3.

		81			
	75	95^+			60
	76	75^+			45

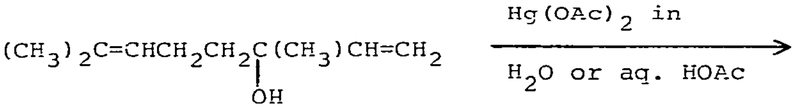
a b

13

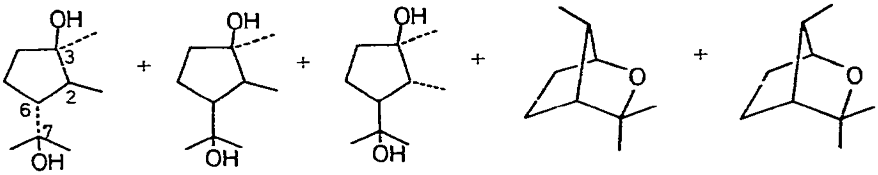
The organomercurials prepared in this study also were oxidized to the secondary alcohols:



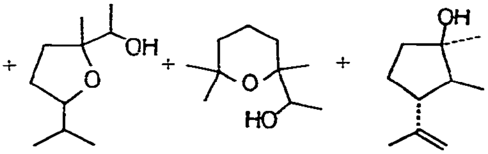
The cyclo-mercuration-demercuration of linalool gave eight products (26):



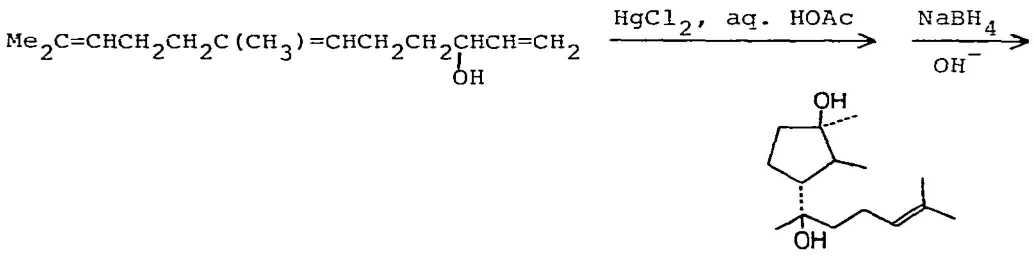
$$(CH_3)_2C{=}CHCH_2CH_2\underset{\displaystyle OH}{\underset{|}{C}}(CH_3)CH{=}CH_2 \xrightarrow[H_2O\text{ or aq. }HOAc]{Hg(OAc)_2\text{ in}}$$



14 15 16 17

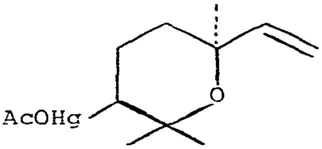


The formation of iridanols (14, 15, 16) occurred in good yield and in better selectivity (56%) and stereoselectivity (85%) than in previous preparations. Similar cyclization of nerolidol was reported by these authors (26):



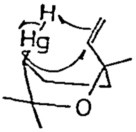
$$Me_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_2CH_2\underset{OH}{C}HCH{=}CH_2 \xrightarrow{HgCl_2,\ aq.\ HOAc} \xrightarrow[OH^-]{NaBH_4}$$

Further work showed the ether products of the oxymercuration of linalool to be derived from a common organomercury intermediate, 18 (27). The C-C bond formation to form the ethers 17 occurred



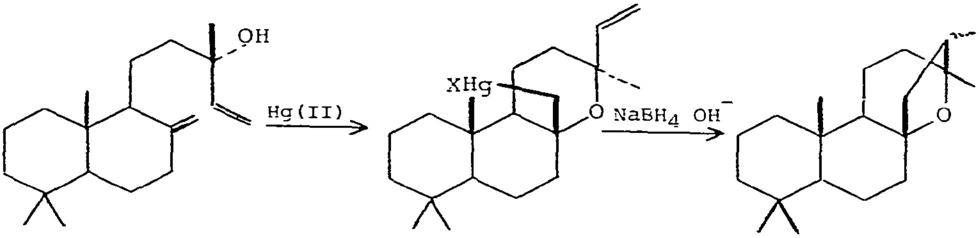
18

during the reduction of 18 with sodium borohydride, probably by direct transfer of hydrogen from mercury to the C=C bond as a result of the close proximity of these functions, as shown in 19.

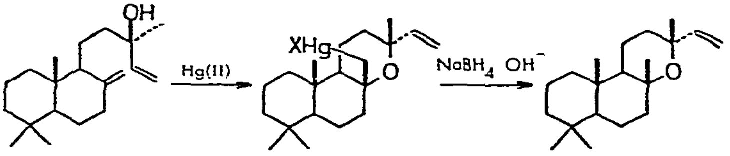


19

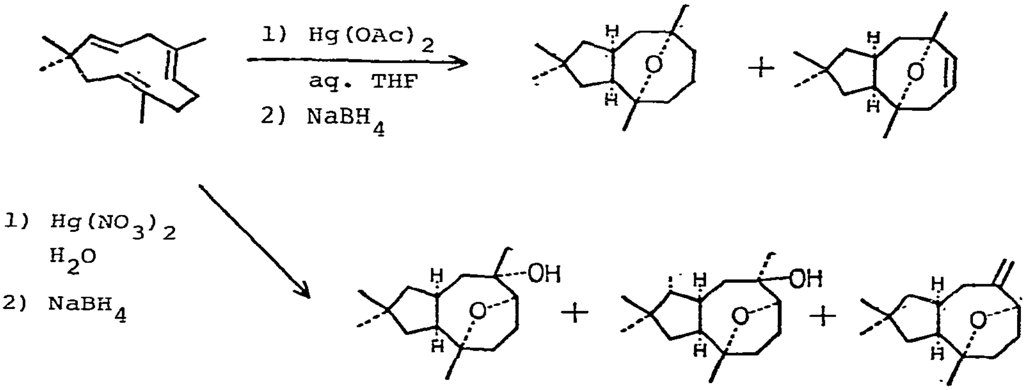
This type of chemistry has been used in a biomimetic cyclization to form the strobane carbon skeleton from 13-epimanool:



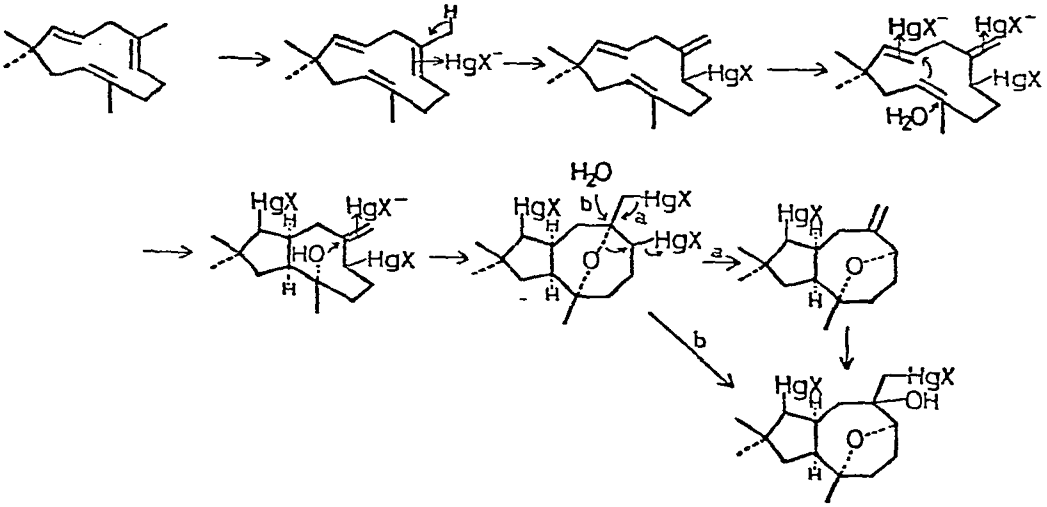
In contrast, an analogous oxymercuration-demercuration of the isomeric manool in which such close approach between the HgH and the vinyl groups is not possible proceeded without such C-C bond formation:



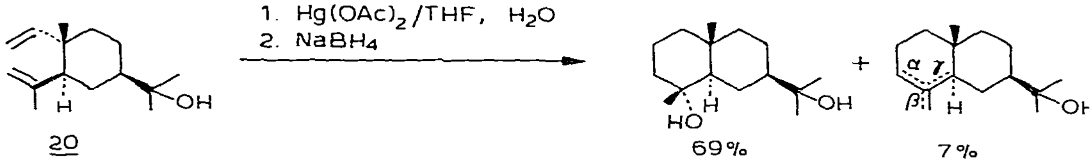
Cyclic ethers also are produced in the oxymercuration of dienes. The oxymercuration of humulene with $Hg(OAc)_2$ in aqueous THF, followed by $NaBH_4$ reduction of the product, gave 3,6-seco-protoilludane derivatives (28):

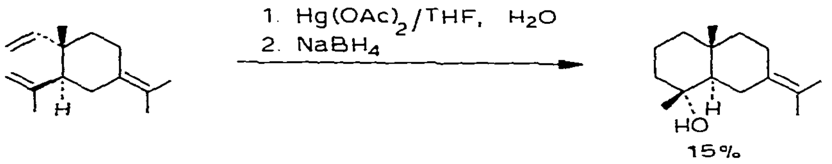


The results of experiments in which $NaBD_4$ was used in the reduction of the organomercury products led to the following suggested mercuration mechanism:

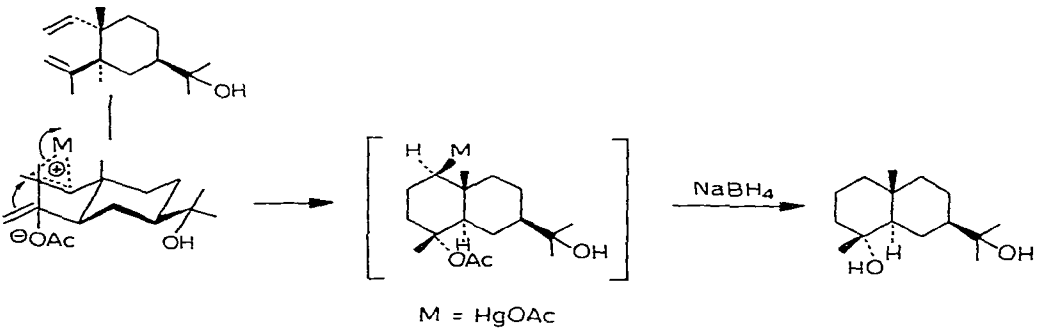


Other examples of diene oxymercuration have been reported from the Firmenich laboratories (29):

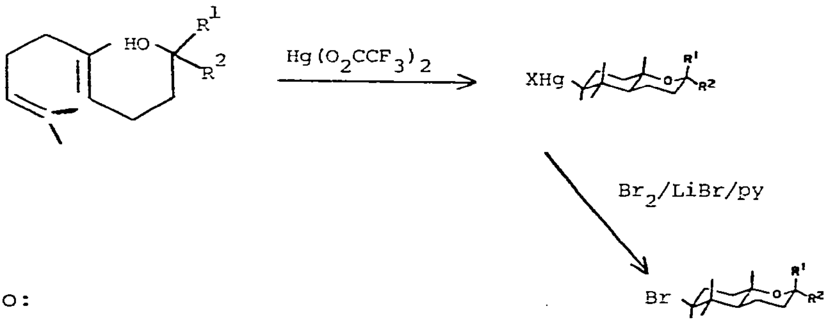




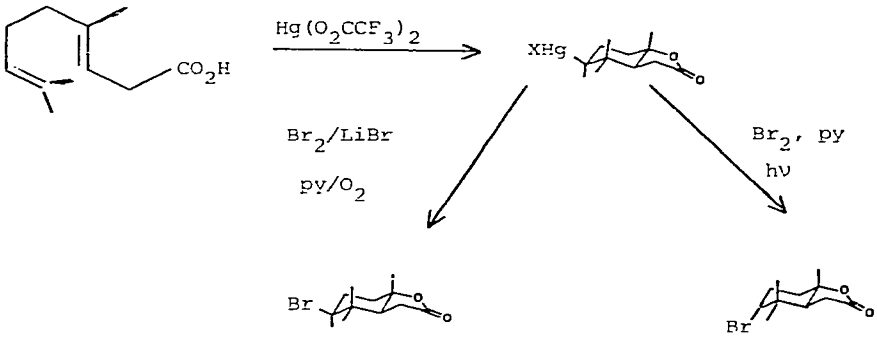
The following mechanism was suggested for this cyclization of elemol, 20



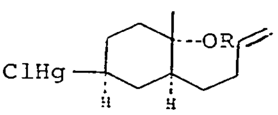
Hoye and Kurth (30) have described cyclizations of diene alcohols *via* mercuration and subsequent bromodemercuration:



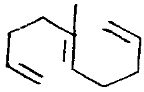
also:



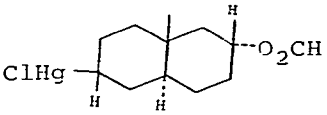
The yields in these reactions were not high (∿10-25%). Further studies of oxidative cyclization of polyenes by mercury(II) salts have been reported by Julia and Fourneron (31). The cyclization of 21, obtained by reaction of 22 with $Hg(OAc)_2$ in formic acid followed by treatment with sodium chloride solution, by the action of formic acid at 20°C, gave 23 as major product. Use of



21 (R = H or C(O)H)

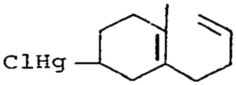


22

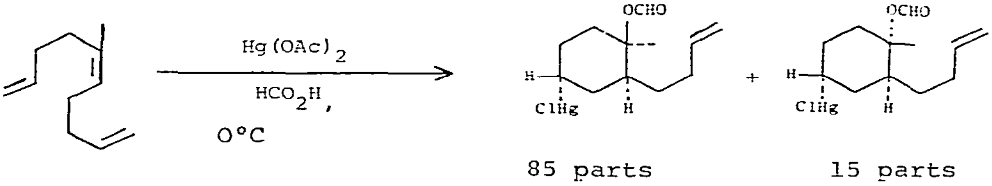


23

DCO_2D in place of HCO_2H did not result in deuterium incorporation in the product. It would appear that mercurated diene 24 is not an intermediate in the cyclization of 21. Also described was the cyclization of triene 25.

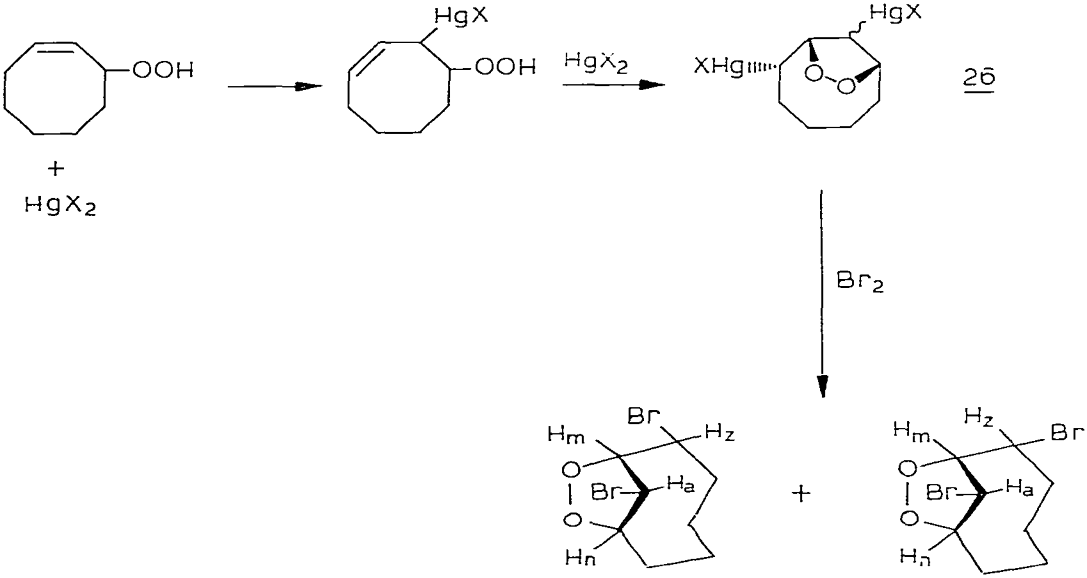


24

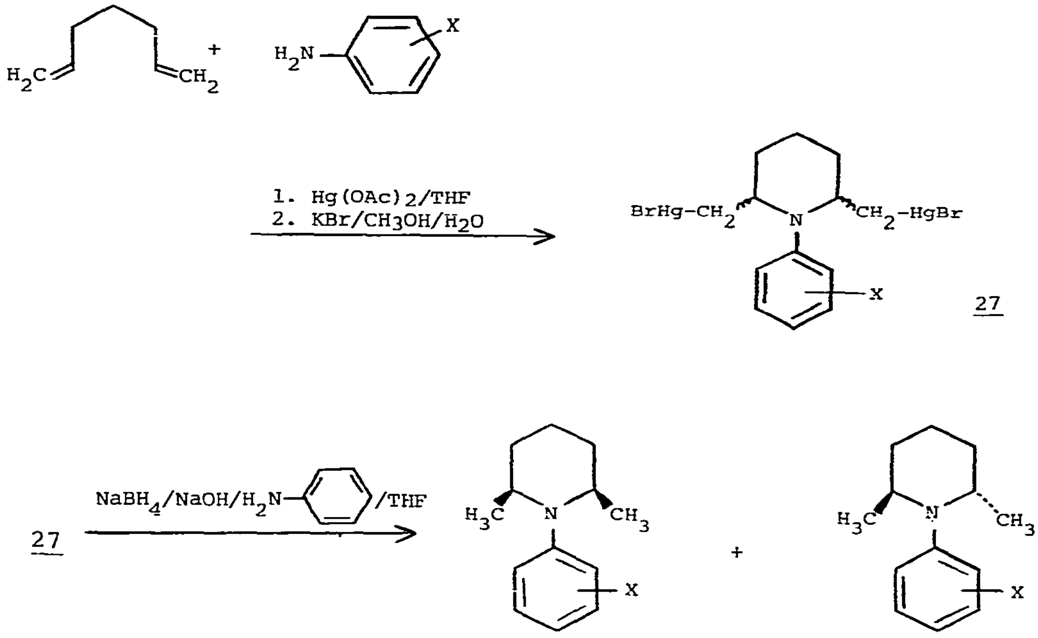


25

Peroxymercuration of 2-cyclooctenyl hydroperoxide with mercuric trifluoroacetate gave a bicyclic product, 26, which was converted to the dibromo derivative without prior isolation (32):



Aminomercuration of 1,6-heptadiene has been used to prepare a number of N-phenylpiperidines(33):

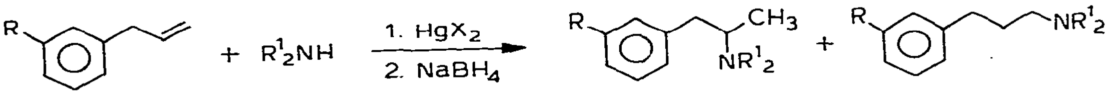


cis- and trans-2,6-Bis[bromomercuriomethyl]-N-arylpiperidines

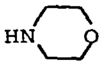
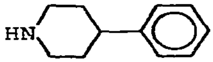
X in 27	Reaction conditions $Ar{-}NH_2/Hg^{2+}$ (mol/mol)	Time	Yield[a] [%]
H	5/1	20 min	95
$4{-}H_3C$	3/1	2.5 h	89
$4{-}H_3CO$	3/1	18 h	88
4-Cl	3/1	75 min	90
$2{-}H_3C$	4/1	18 h	92

[a] Based on diene 1.

Reduction of these mercurials gave the 2,6-dimethylpiperidines in which the cis isomer predominated by a wide margin. Aminomercuration-demercuration also has been used to good advantage in the synthesis of N-substituted N-methylphenethylamines (34):

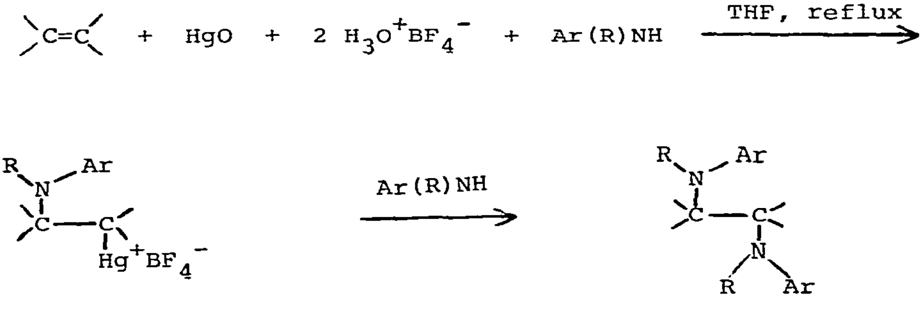


28 29

R	amine (NR^1_2)	28/29	isolated yield, %
OCH_3	$NH_2CH_2CH(OEt)_2$	100/0	87
OCH_3	$NH_2CH_2CH_2CH_2CH_3$	100/0	48
OCH_3	NH_2CH_2Ph	90/10	78
OCH_3	$NH(CH_2CH_3)_2$	60/40	39
OCH_3	NH_2Ph	100/0	41
OCH_3		100/0	68
OCH_3		80/20	86
H	NH_2CH_2Ph	90/10	71
CF_3	NH_2CH_2Ph	100/0	57
OCH_3	$NH_2CH_2CH_3{}^{b,a}$	80/20	87
CF_3	$NH_2CH_2CH_3{}^{b,a}$	82/18	93
CF_3	$NH_2CH_2CH(OEt)_2$	90/10	62

[a] $Hg(ClO_4)_2$ substituted for $Hg(NO_3)_2$. [b] 30% aqueous ethylamine.

The 1,2-diamination of olefins can be effected readily in a "one-pot" process by reaction of an olefin with a mixture of tetrafluoroboric acid and mercuric oxide in the presence of an excess of a primary or secondary aromatic amine (35):



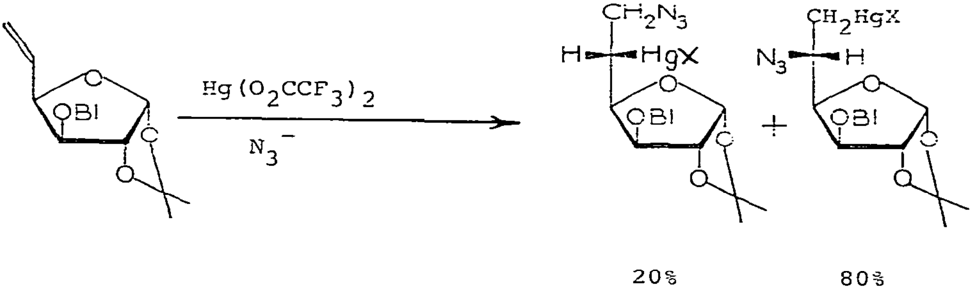
30

As Table 4 shows, the diamine yields are quite good.

Table 4. Diamination of Olefins Using the HgO/Tetrafluoroboric Acid Reagent.

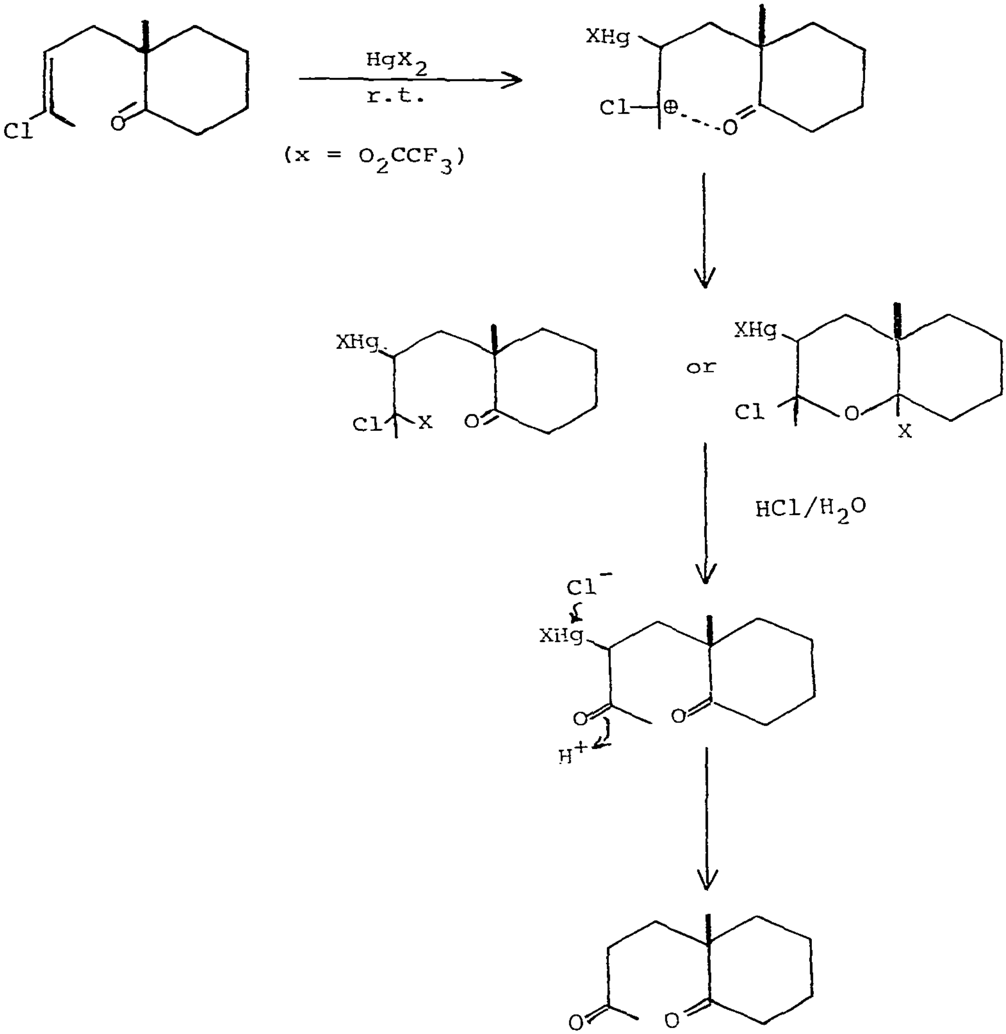
Alkene	Amine	30, Yield [%]
propene	aniline	62
1-heptene	aniline	70
cyclohexene	aniline	89
cyclooctene	aniline	80
styrene	aniline	69
allylbenzene	aniline	88
styrene	o-toluidine	95
styrene	N-methylaniline	65

The azidomercuration reaction has been applied to the synthesis of amino-sugars (36):



Demercuration of the products by treatment with KBH_4/KOH gave the azido-sugar. The known 5-amino-5,6-dideoxy-1,2-O-isopropylidene-α-D-gluco-furannose was obtained by reduction of the N_3 function to NH_2 and hydrogenolysis of the benzyl group by catalytic hydrogenation.

Organomercury intermediates are involved in the conversion of α-(3-chloro-2-butenyl)- and α-(2-chloroallyl)-ketones to 1,5- and 1,4-diketones, respectively, by the action of mercuric trifluoroacetate in nitromethane, dichloromethane or benzene, e.g. (37):



(97%)

The vinylic chlorides which were hydrolyzed in this manner included:

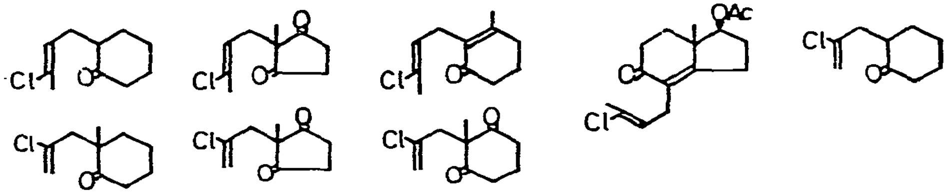
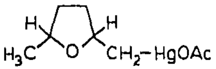
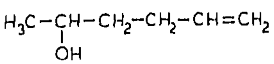
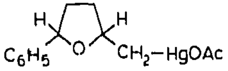
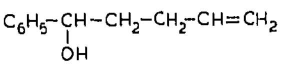
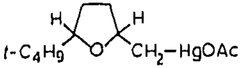
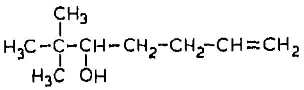
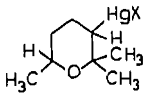
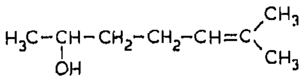
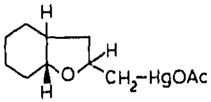
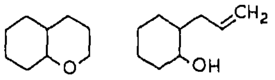
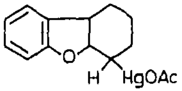
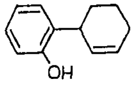
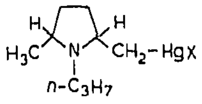
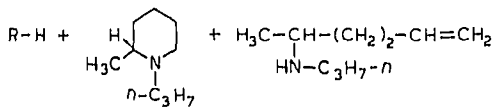
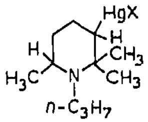
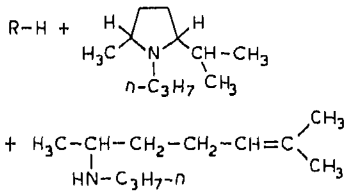
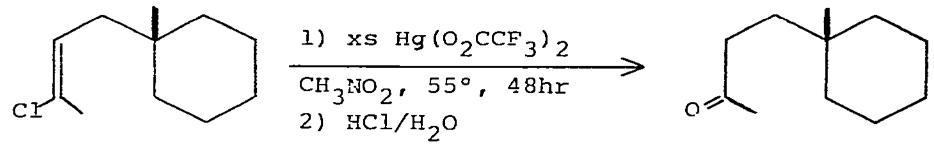


Table 5. Reductive Demercuration by Phase Transfer Catalysis Technique (38).

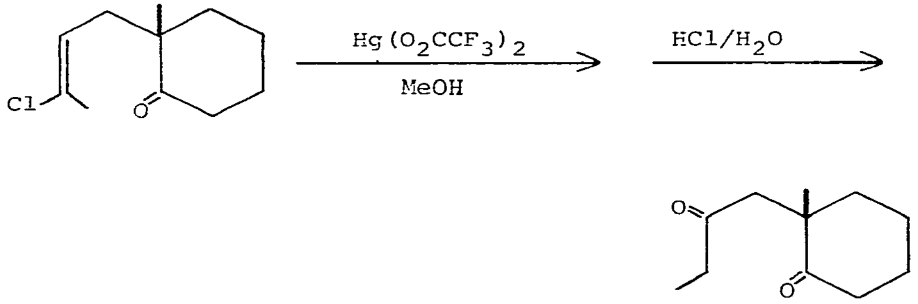
Organomercury Compounds	Demercuration Products	Classical Reduction		Reduction under Phase-transfer Conditions	
		Time	Yield (%)	Yield (%) of R-H	Remarks
	R-H +  $H_3C-\underset{OH}{CH}-CH_2-CH_2-CH=CH_2$	a few hours	40	98	2% alcohol
	R-H +  $C_6H_5-\underset{OH}{CH}-CH_2-CH_2-CH=CH_2$	a few hours	60	100(85)	
	R-H +  $H_3C-\underset{H_3C}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_2-CH_2-CH=CH_2$	a few hours	45	100(85)	
	R-H +  $H_3C-\underset{OH}{CH}-CH_2-CH_2-CH=C(CH_3)_2$	a few hours	60	98	2% alcohol
	R-H + 	1 h	60	83	10% hexahydro-chromane + 7% alcohol
	R-H + 	a few hours	50	90	10% phenol

	 $H_3C-\underset{HN-C_3H_7-n}{\underset{\vert}{CH}}-(CH_2)_2-CH=CH_2$	30 min	40	83	17% piperidine
	 $+\ H_3C-\underset{HN-C_3H_7-n}{\underset{\vert}{CH}}-CH_2-CH_2-CH=C(CH_3)_2$	30 min	20	100	

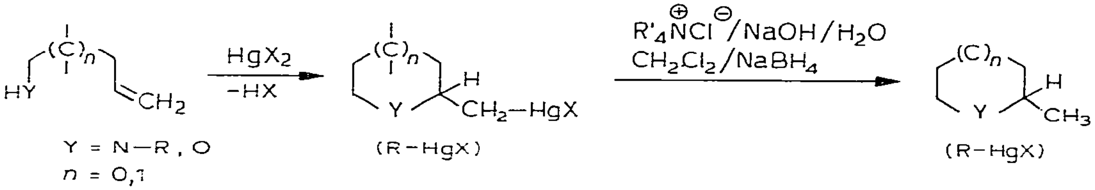
When the vinylic chloride did not contain a ketone function, its hydrolysis by this procedure was much more difficult:



Surprisingly, the use of mercuric trifluoroacetate in methanol medium resulted in formation of the ethyl ketone as the main product, rather than the methyl ketone:



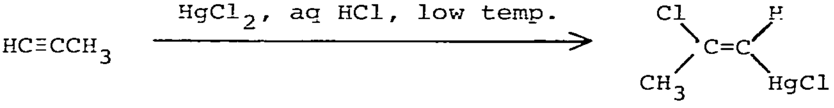
Finally, a point of methodology: The reduction of olefin solvomercuration products with sodium borohydride can be effected by the phase transfer catalysis technique (38):



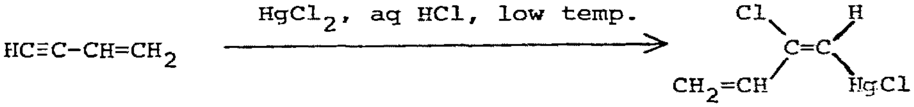
In this procedure the rates are rapid and rearrangements are minimized. Table 5 presents some results.

B. <u>Acetylenes</u>

The chloromercuration of some acetylenes has been reported (39):

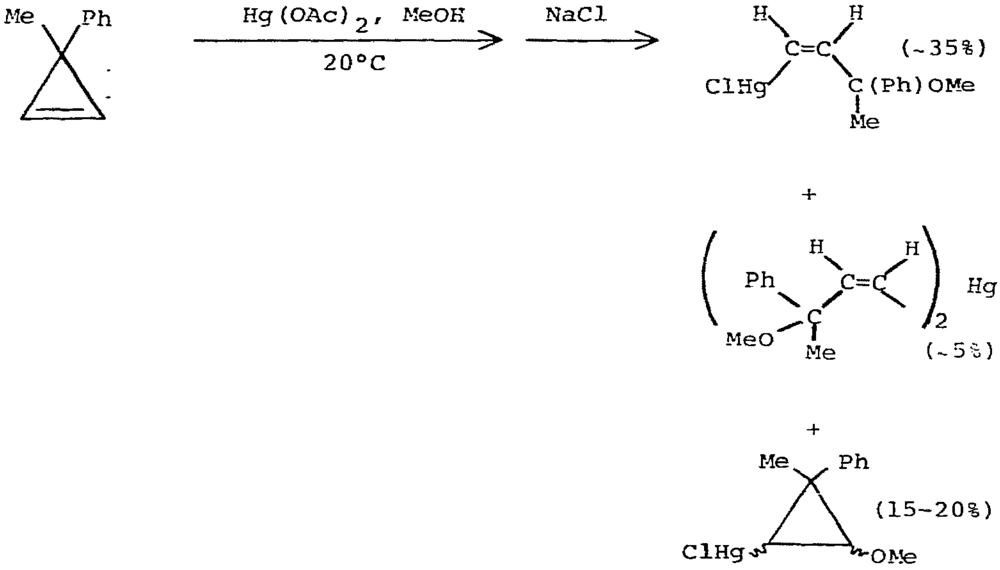


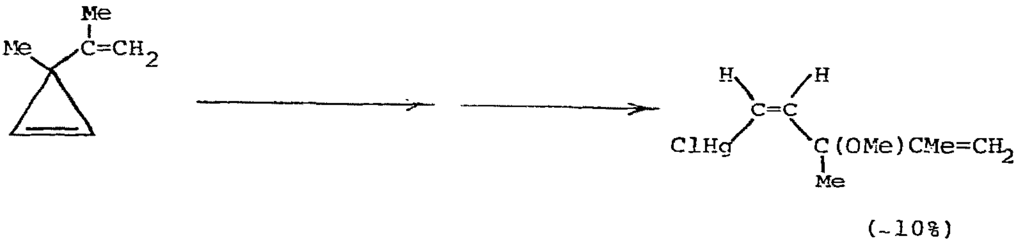
(The product is unstable in air under ambient conditions, but can be kept at -5° to -10°C.)



C. Cyclopropanes and Cyclopropenes

The methoxymercuration of 3-methyl-3-phenyl- and 3-methyl-3-isopropenylcyclopropene resulted in substantial ring opening (40):

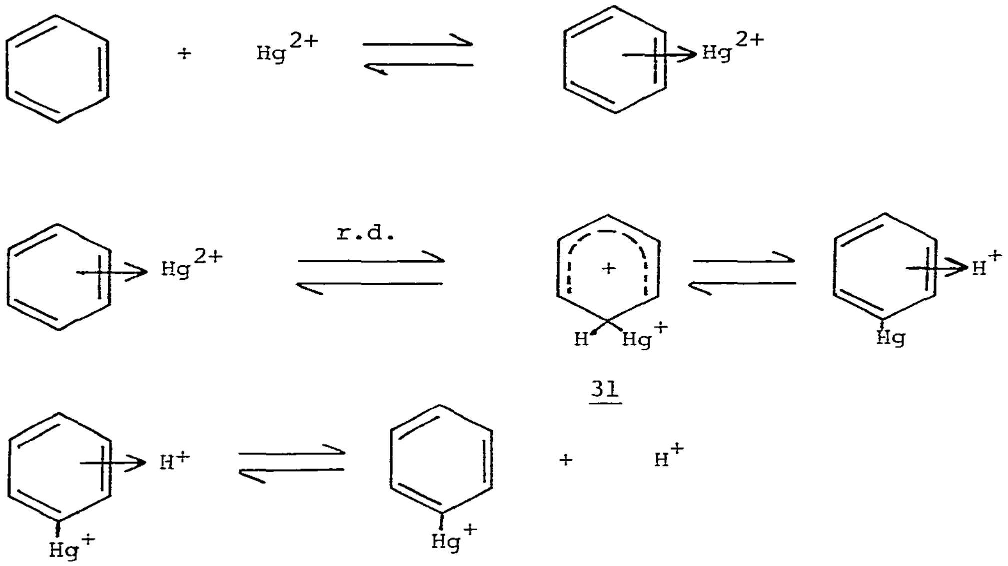




Electrocyclic ring-opening of the cyclopropyl cation formed by addition of $AcOHg^+$ to the C=C bond was held responsible for the formation of acyclic products.

D. Aromatic Compounds

The initial steps in the mercuration of aromatic compounds have been postulated to be the formation of Hg(II)-arene complexes:



31

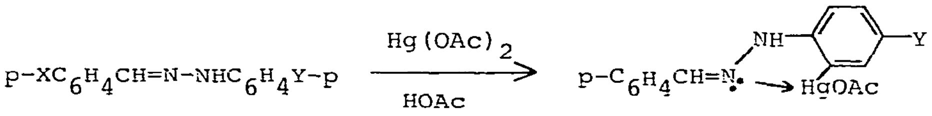
Table 6.

SOME MERCURY(II)-ARENE COMPLEXES

Complex	Color
$Hg(SbF_6)_2\cdot(Benzene)_2$	colorless
$Hg(SbF_6)_2\cdot(Toluene)_2$	colorless
$Hg(SbF_6)_2\cdot(p\text{-}Xylene)_2$	yellow
$Hg(SbF_6)_2\cdot(Mesitylene)_2$	yellow
$Hg(SbF_6)_2\cdot(Durene)_2$	yellow
$Hg(AsF_6)_2\cdot(Durene)_2$	yellow
$Hg(SbF_6)_2\cdot(Pentamethylbenzene)_2$	yellow
$Hg(AsF_6)_2\cdot(Pentamethylbenzene)_2$	yellow
$Hg(SbF_6)_2\cdot(Hexamethylbenzene)_2$	yellow
$Hg(CF_3COO)_2\cdot(Hexamethylbenzene)$	colorless
$Hg(SbF_6)_2\cdot(Naphthalene)$	yellow
$Hg(SbF_6)_2\cdot(Naphthalene)_2$	orange
$Hg(AsF_6)_2\cdot(Naphthalene)_2$	orange
$Hg(SbF_6)_2\cdot(Phenanthrene)$	orange
$Hg(SbF_6)_2\cdot(Biphenyl)_2$	orange
$Hg(SbF_6)_2\cdot(Biphenyl)$	yellow

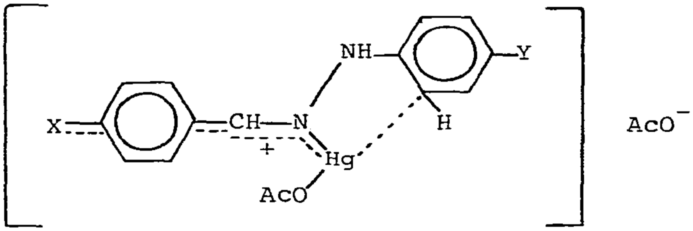
The first actual isolation of such arene-Hg(II) complexes by Damude and Dean was cited in last year's organomercury Annual Survey. Full details of this work now have been reported (41). Table 6 shows the complexes of type Hg(arene)$^{2+}$ and Hg(arene)$_2$$^{2+}$ which were isolated as stable hexafluoroarsenate, hexafluoroantimonate or trifluoroacetate salts. These were prepared by reactions of the respective arene with strong acid salts of Hg(II) in liquid sulfur dioxide. All were isolated and analyzed. On the basis of NMR experiments, principally the values of ^{199}Hg-^{13}C coupling constants, it was concluded that the Hg(arene)$^{2+}$ species are σ-bonded ions of type 31.

Substituted benzaldehyde phenylhydrazones reacted with mercuric acetate in acetic acid; aromatic ring mercuration occurred solely at the *ortho*-position of the N-phenyl ring (42):



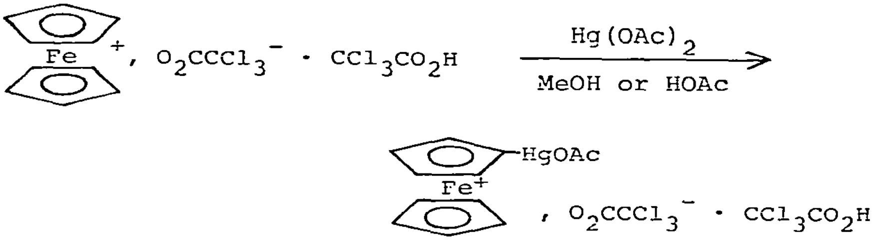
X	Y	Product Yield (%)
MeO	Br	72
Me	Br	70
H	Br	75
Cl	Br	82.5
Br	Br	
NO_2	Br	90
MeO	NO_2	88
Me	NO_2	78
H	NO_2	78
Cl	NO_2	35
Me	H	
Me	MeO	
NO_2	MeO	48
NO_2	H	86
NO_2	NO_2	
Benzophenone		55

A transition complex of type 32 in which the β-nitrogen directs the HgOAc$^+$ moiety to the *ortho*-position was suggested on the basis of the results of studies of the effects of substitutents on the reaction rate.

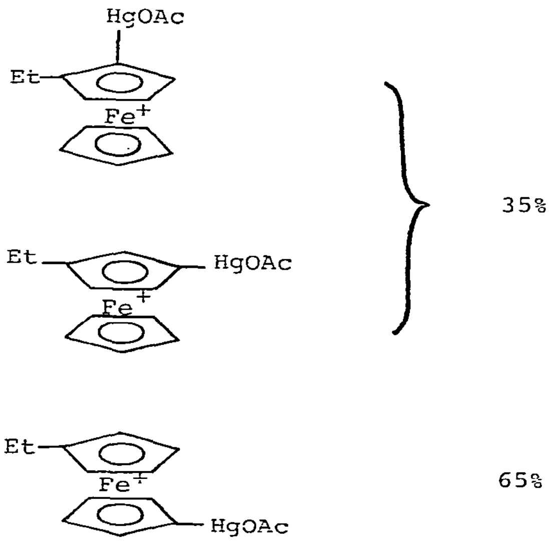


32

Although neutral ferrocenes have been mercurated, there has been no report of the mercuration of a positively charged ferrocenium salt until the recent study by Floris and Illuminati (42a). Surprisingly, ferrocenium trichloroacetate is mercurated by mercuric acetate at a rate which is of the same order of magnitude as that of ferrocene mercuration:



Mercuration of ethyl- and 1,1'-diethylferrocenium trichloroacetates occurred at comparable rates. In the mercuration of the ethylferrocenium salt three isomeric products were formed:



The isomer distrubution was established by reduction of the mixture of ferrocenium salts produced in the mercuration reaction with zinc powder, bromodemercuration of the ferrocenes thus obtained with N-bromosuccinimide and examination of the ethylbromoferrocene mixture which resulted by GLC and NMR.

Hg(II) salt-catalyzed nitration of benzene derivatives involves organomercury intermediates, as has been shown previously (1977) by Stock and Wright:

$$CH_3C_6H_5 + Hg(OAc)_2 \longrightarrow CH_3C_6H_4HgOAc + HOAc$$

$$CH_3C_6H_4HgOAc + NO^+ \longrightarrow CH_3C_6H_4NO + HgOAc^+$$

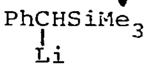
$$CH_3C_6H_4NO + HNO_3 \longrightarrow CH_3C_6H_4NO_2 + HNO_2$$

A study of the isomer distributions in the $Hg(OAc)_2$-catalyzed nitration of eight benzene derivatives showed that in the reactions of the more nucleophilic alkylbenzenes, which proceed in good yield, the o/m/p ratios are very similar to those obtained in the mercuration of these arenes. This was not the case for the relatively deactivated halobenzenes (43).

4. THE USE OF ORGANOMERCURY COMPOUNDS IN SYNTHESIS.

A. Synthesis of Organometallic Compounds

The displacement of mercury from its organic compounds by a different metal is a long-known preparative procedure for organometallic compounds. New examples of such reactions have been reported.



$$\begin{tikzcd}
(PhCH_2SiMe_2CH_2)_2Hg \arrow[r, "Li/MeTHF", "(ref.\ 44)"'] & \underset{33}{PhCH_2SiMe_2CH_2Li} \arrow[d, "50^\circ C"] \\
 & \underset{\mathrm{Li}}{\mathrm{PhCHSiMe_3}} \quad 34
\end{tikzcd}$$

In THF and DME the rearrangement of 33 to 34 was rapid and only 34 could be detected by ^{13}C NMR spectroscopy.

$$(Me_3SiCH_2)_2Hg \xrightarrow[\text{(in an ultrasonic bath)}]{\text{M, 0°C, THF, MeTHF or DME}} Me_3SiCH_2M$$

(M = Li, Na, K, Rb, Cs)

(ref. 44)

The Me_3SiCH_2M reagents were used to metalate various weakly acidic hydrocarbons and these were present in the reaction mixture when the organoalkali reagents were prepared.

$$(PhCH_2)_2Hg \xrightarrow[\text{(ref. 44)}]{\text{M, - 30°C}} PhCH_2M \quad (M = Li,\ Na)$$

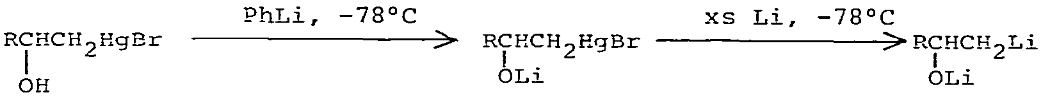
$$(C_2H_5)_2Hg \xrightarrow[\text{(ref. 45)}]{\text{Li (vapor phase)}} \text{"}C_2Li_6\text{"}$$

The evidence for the formation of "C_2Li_6" is the almost exclusive formation of C_2D_6 by treatment of the solid reaction product with D_2O (45). Curiously, similar reactions of $(CF_3)_2Hg$, $(CH_3)_2Hg$ and ICH_2HgI with lithium vapor (from a Knudsen cell at 800°C) gave two-carbon organic compounds, C_2D_6, C_2D_4 and C_2D_2, after hydrolysis of the reactions products.

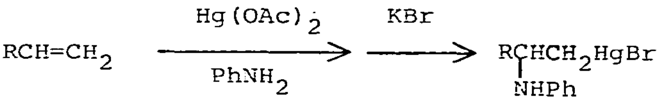
Interesting and useful β-functional alkyllithium reagents, $LiO\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Li$ and $PhN(Li)\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Li$, were prepared by metal displacement from olefin oxy- and aminomercuration products (46):

$$RCH{=}CH_2 \xrightarrow[\text{aq. THF}]{Hg(OAc)_2} \xrightarrow{\text{aq. KBr}} R\underset{\underset{OH}{|}}{C}HCH_2HgBr$$

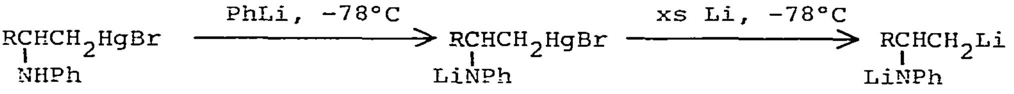
(R = H, Me, Ph)



$$R\underset{\underset{OH}{|}}{C}HCH_2HgBr \xrightarrow{\text{PhLi, -78°C}} R\underset{\underset{OLi}{|}}{C}HCH_2HgBr \xrightarrow{\text{xs Li, -78°C}} R\underset{\underset{OLi}{|}}{C}HCH_2Li$$



$$RCH{=}CH_2 \xrightarrow[PhNH_2]{Hg(OAc)_2} \xrightarrow{\text{KBr}} R\underset{\underset{NHPh}{|}}{C}HCH_2HgBr$$



$$R\underset{\underset{NHPh}{|}}{C}HCH_2HgBr \xrightarrow{\text{PhLi, -78°C}} R\underset{\underset{LiNPh}{|}}{C}HCH_2HgBr \xrightarrow{\text{xs Li, -78°C}} R\underset{\underset{LiNPh}{|}}{C}HCH_2Li$$

The metal displacement reaction also has been applied to the synthesis of triarylgallium and -indium compounds (47):

$$3\ Ar_2Hg + 2\ M \longrightarrow 2\ Ar_3M + 3\ Hg$$

Table 7.

SYNTHETIC DATA FOR TRIARYL-GALLIUM (47) AND -INDIUM COMPOUNDS

Compound	Method	Yield (%) [a]
$(C_6H_5)_3Ga$	A, B	88
$(2\text{-}CH_3C_6H_4)_3Ga$	B	89
$(3\text{-}CH_3C_6H_4)_3Ga$	B	49
$(4\text{-}CH_3C_6H_4)_3Ga$	B	92
$(4\text{-}C_2H_5C_6H_4)_3Ga$	B	58
$[4\text{-}(CH_3)_3CC_6H_4]_3Ga$	B	84
$(4\text{-}CH_3OC_6H_4)_3Ga$	B	73
$(3\text{-}FC_6H_4)_3Ga$	B	80
$(4\text{-}FC_6H_4)_3Ga$	B	98
$(2\text{-}ClC_6H_4)_3Ga$	B	65
$(3\text{-}ClC_6H_4)_3Ga$	B	59
$(4\text{-}ClC_6H_4)_3Ga$	B	40
$(3\text{-}BrC_6H_4)_3Ga$	B	22
$(4\text{-}BrC_6H_4)_3Ga$	B	38
$(C_6H_5)_3In$	A,B	78
$(2\text{-}CH_3C_6H_4)_3In$	B	70
$(3\text{-}CH_3C_6H_4)_3In$	B	65
$(4\text{-}CH_3C_6H_4)_3In$	B	90
$(4\text{-}C_2H_5C_6H_4)_3In$	A,B	52
$[4\text{-}(CH_3)_3CC_6H_4]_3In$	B	87
$(4\text{-}CH_3OC_6H_4)_3In$	B	68
$(3\text{-}FC_6H_4)_3In$	B	71
$(4\text{-}FC_6H_4)_3In$	B	85
$(4\text{-}ClC_6H_4)_3In$	B	31

[a] Based on R_2Hg as limiting reagent.

Table 7 gives results. (Method A involves heating the reactants at 150°C (no solvent) for 48 hr.; Method B, heating them in refluxing toluene solution for 60 hr.).

Of special interest is the high yield preparation of organic derivatives of ytterbium and europium using the metal displacement procedure (48):

$$Ar_2Hg + M \xrightarrow{THF/r.t.} Ar_2M + Hg$$

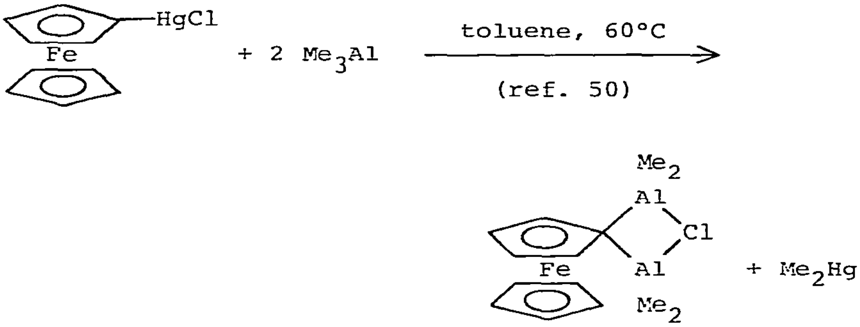
(Ar = C_6F_5 and o- and p-HC_6F_4 for M = Yb; Ar = C_6F_5 for M = Eu)

$$(PhC{\equiv}C)_2Hg + Yb \xrightarrow{THF/r.t.} (PhC{\equiv}C)_2Yb + Hg$$

Organic group exchange between organomercurials and organic derivatives of other metals also serves in organometallic syntheses. Such transmetalations have been reported in 1978/79 for organic compounds of zinc, aluminum and gold.

$$(CF_3)_2Hg + (CH_3)_2Zn \xrightarrow[\text{(ref. 49)}]{\text{pyridine, r.t.}} CH_3ZnCF_3 + (CF_3)_2Zn$$

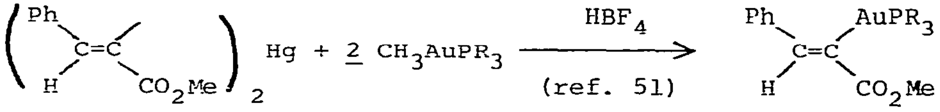
(an NMR study)



(structure established by X-ray diffraction)

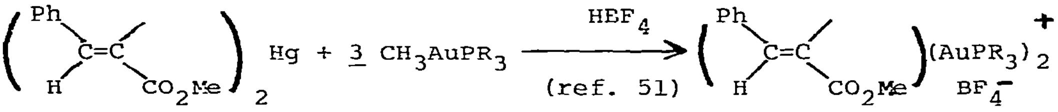
$$\underset{\text{(cis isomer)}}{(PhCH{=}CH)_2Hg} + 2\ CH_3AuPR_3 \xrightarrow[\text{(ref. 51)}]{HBF_4} [(cis\text{-}PhCH{=}CH)(AuPR_3)_2]BF_4$$

(R = Ph, $C_5H_5FeC_5H_4$)



(R = Ph, $C_5H_5FeC_5H_4$)

but:



$(R = C_5H_5FeC_5H_4)$

Several examples have been reported of another synthetic procedure involving organomercurials: the replacement of inorganic (halo, carboxy, etc.) substituents on a main group or transition metal by organic groups from the mercurial.

Organolead carboxylates: (52):

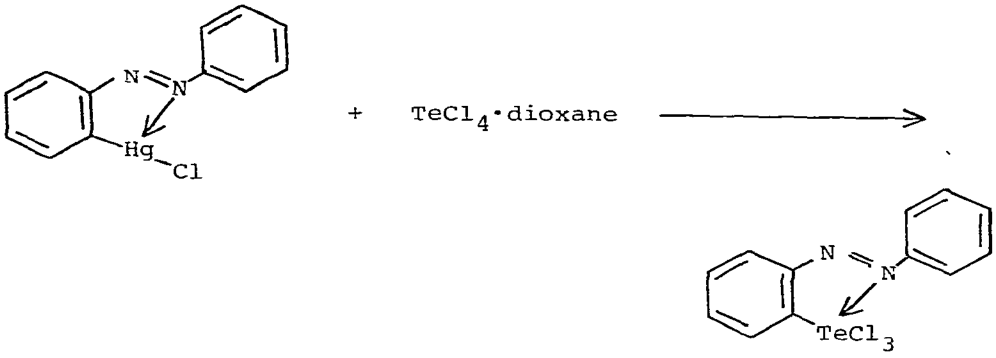
$$Ar_2Hg + Pb(O_2CCH_3)_4 \xrightarrow{\text{chloroform, r.t.}} ArPb(O_2CCH_3)_3 + ArHgO_2CCH_3$$

$(Ar = o\text{-}MeC_6H_4,\ m\text{-}MeOC_6H_4)$

$$(ArHgO_2CCF_3 + Pb(O_2CCF_3)_4 \xrightarrow{CF_3CO_2H} ArPb(O_2CCF_3)_3 + Hg(O_2CCF_3)_2$$

$(Ar = m,\ p\text{-}CF_3C_6H_4{:}\ \ 3,5\text{-}(CF_3)_2C_6H_3$

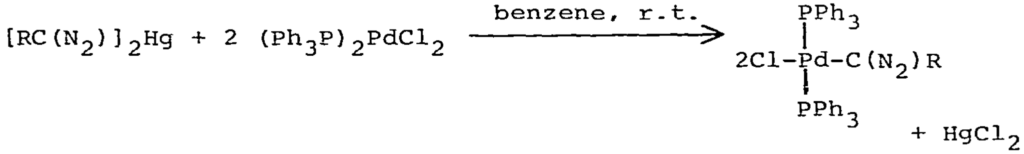
Organotellurium compounds (53):



A phenylvanadium compound (54):

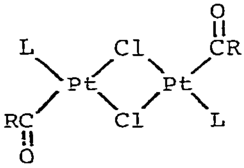
$$Ph_2Hg + VOCl_2(OCHMe_2) \xrightarrow{\text{pentane, }-10°C} PhVOCl(OCHMe_2) + PhHgCl$$

A diazoalkylpalladium complex (55):

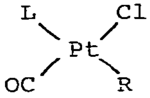


$$[RC(N_2)]_2Hg + 2\ (Ph_3P)_2PdCl_2 \xrightarrow{\text{benzene, r.t.}} 2Cl\text{-}\overset{\displaystyle PPh_3}{\underset{\displaystyle PPh_3}{Pd}}\text{-}C(N_2)R + HgCl_2$$

The action of diphenylmercury on cis-$PtCl_2(CO)PMePh_2$ in chloroform gave the benzoylplatinum complex 35 (56). In solution 35 is in equilibrium with 36. Similar reactions were carried out with Me_2Hg, Et_2Hg and $(PhCH_2)_2Hg$. In the case of the first two, compounds

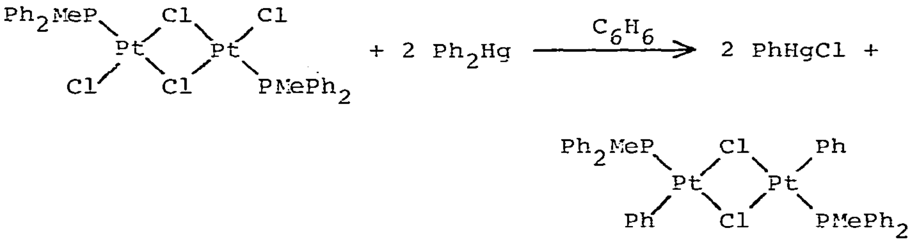


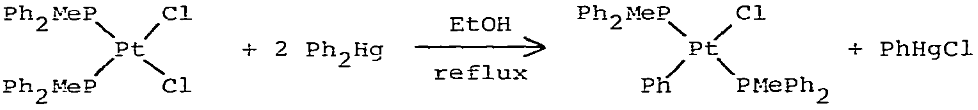
35 L = $PMePh_2$
R = Ph



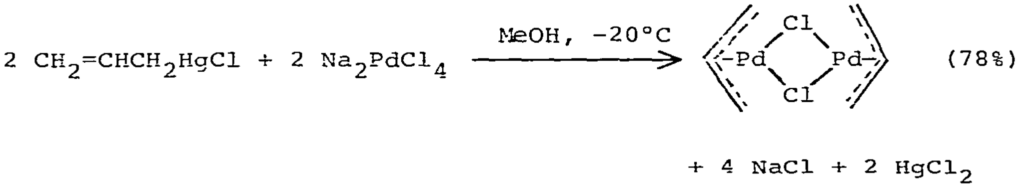
36

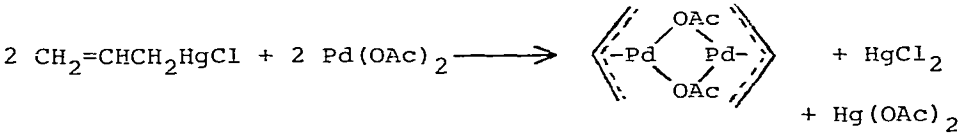
analogous to 35 (R = Me and Et) were the solid products which were isolated, but the solid obtained with dibenzylmercury was 36, with R = $PhCH_2$ and L = $PMePh_2$. Also reported were the reactions:



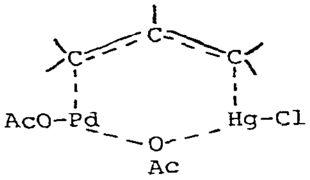


Palladium(II) salts react with allylic mercuric halides to give π-allylpalladium complexes (57):



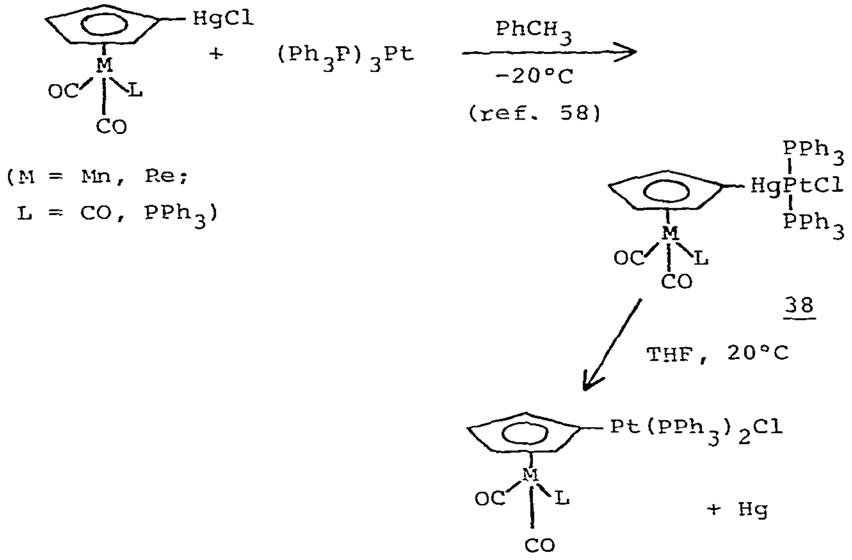


In the reactions of $(NH_4)_2PdCl_4$ and K_2PdBr_4 with allylmercuric chloride and bromide, respectively, products of type $C_3H_5PdCl \cdot HgCl_2$ and $C_3H_5PdBr \cdot HgBr_2$ were obtained. An S_Ei mechanism (transitione state 37) was suggested for these exchange reactions.

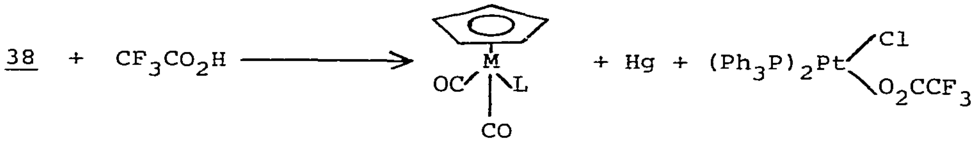


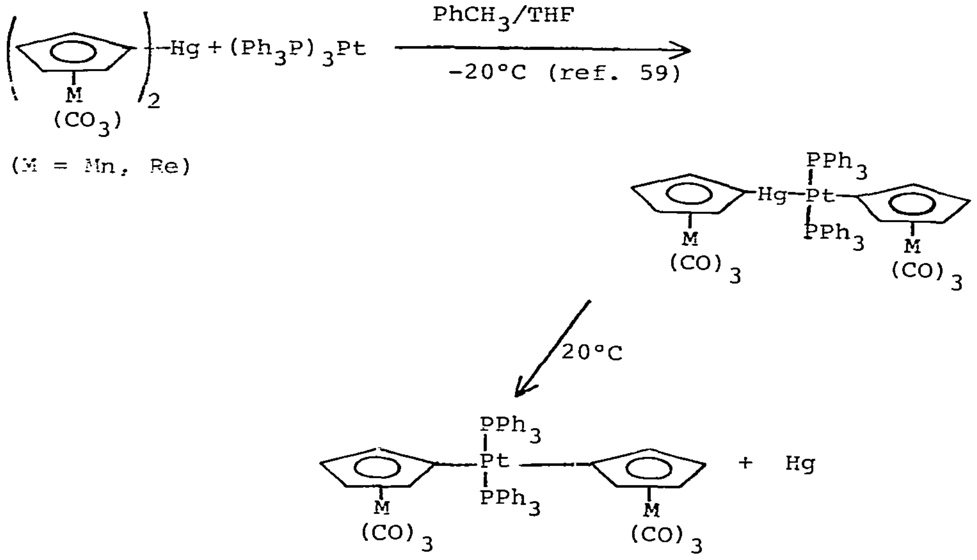
37

Oxidative addition processes involving organomercurials and zerovalent palladium and platinum complexes also have been investigated. In most cases, the initially formed, mercury-containing products were not stable and underwent demercuration at room temperature (58, 59):



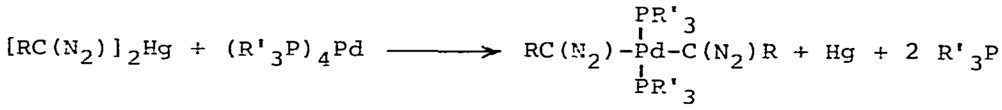
Complexes of type 38 are destroyed by trifluoroacetic acid:





(M = Mn, Re)

Also (55):

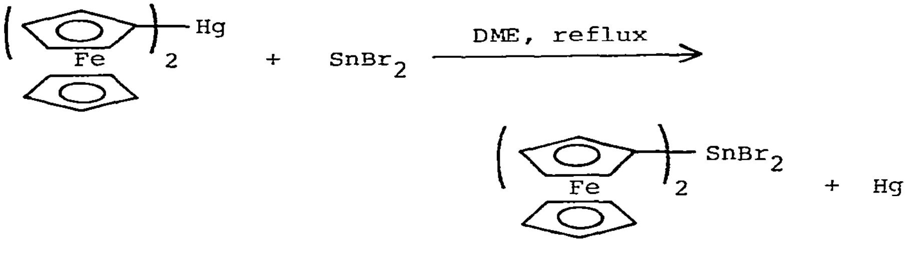


$$[RC(N_2)]_2Hg + (R'_3P)_4Pd \longrightarrow RC(N_2)-\underset{PR'_3}{\overset{PR'_3}{Pd}}-C(N_2)R + Hg + 2\ R'_3P$$

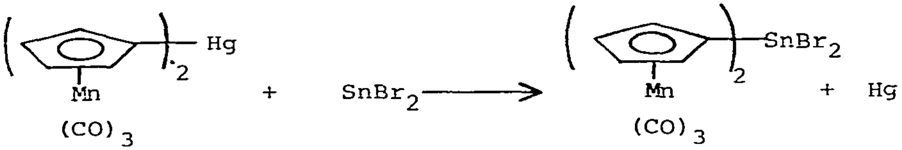
Examples were described for the following cases:

R	R'
CO_2Et	Ph
CO_2Et	Et
C(O)Me	Ph
Ph	Et

A similar oxidative addition reaction occurred with a main group substrate (60):

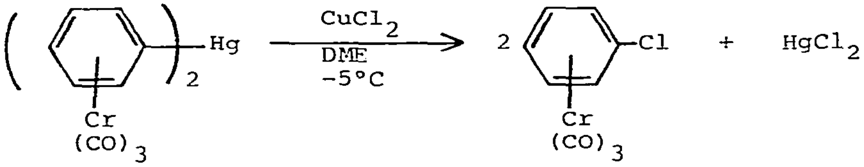


(80%)

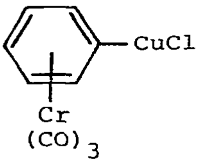


B. Applications in Organic Synthesis

Organomercurial halogenolysis, which has been used often in the preparation of organic halides, has been applied to the synthesis of chlorobenzene-chromium tricarbonyl (61):



(97%)



39

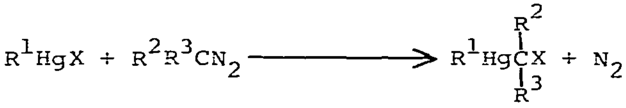
An organocopper intermediate, 39, was suggested.

Mercury-carbon bond cleavage to give organic products occurred when acetoxymercuripyruvaldehyde diethyl acetal was treated with acetyl chloride (61a):

$$AcOHgCH_2C(O)CH(OEt)_2 + CH_3C(O)Cl \xrightarrow[r.t.]{CHCl_3} CH_2{=}C(OAc)CH{=}O + CH_3C(O)CH_2C(O)CH(OEt)(OAc)$$

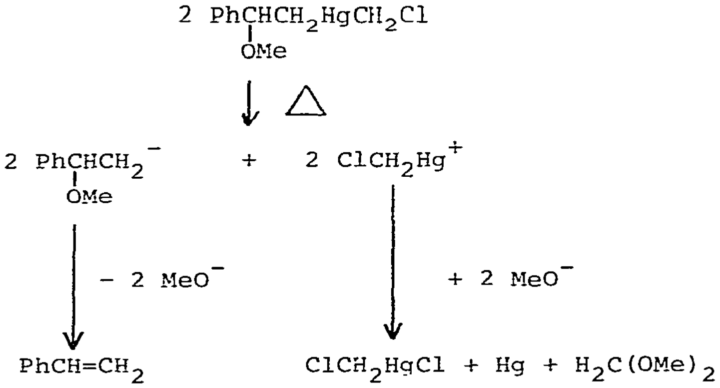
The 2-acetoxyacrolein obtained had $CH_2{=}C(OAc)CH(OEt)_2$ as its precursor, while the second product resulted from cleavage of $ClHgCH_2C(O)CH(OEt)_2$ by acetyl chloride.

α-Haloalkylmercury compounds, previously used as divalent carbon transfer agents, have found other uses in organic synthesis. A number of such compounds has been prepared by the reaction of organomercuric halides with diazoalkanes by Spanish workers (62):

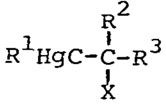
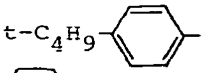
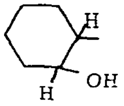
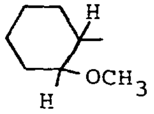


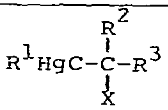
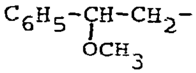
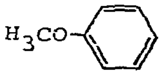
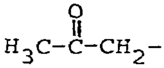
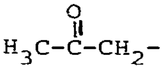
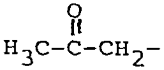
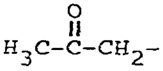
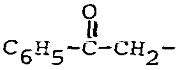
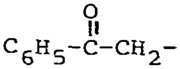
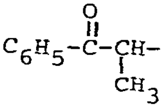
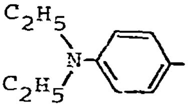
$$R^1HgX + R^2R^3CN_2 \longrightarrow R^1Hg\overset{R^2}{\underset{R^3}{C}}X + N_2$$

In view of the limited stability of some of these compounds, the reaction temperature is a critical factor (Table 8). Their stability as a function of R^1 decreases in the order alkyl~aryl>2-alkoxyalkyl>2-oxoalkyl>2-hydroxyalkyl. Their decomposition gives the haloalkylmercuric halide, elemental mercury and organic products, e.g.:



Preparation of 1-Haloalkylmercury(II) Compounds (62)

 $R^1HgC-\underset{X}{\overset{R^2}{C}}-R^3$				Reaction temperature	Yield [%]
R^1	X	R^2	R^3		
$H_3C-\underset{Cl}{CH}-$	Cl	H	CH_3	+ 5°	95[b]
$C_2H_5-\underset{Cl}{CH}-$	Cl	H	C_2H_5	+ 5°	99[b]
n-C_3H_7	Br	H	H	+ 5°	85[a]
 $t-C_4H_9-C_6H_4-$	Cl	H	H	+ 5°	80[a]
	Cl	H	H	+10°	93[c]
$C_6H_5-\underset{OH}{CH}-CH_2-$	Cl	H	H	+10°	98[b]
$HO-CH_2-CH_2-$	Br	H	H	0°	88[c]
$H_3C-\underset{OH}{CH}-CH_2-$	Br	H	H	+ 5°	91[c]
$C_2H_5-\underset{OH}{CH}-CH_2-$	Br	H	H	+ 5°	93[c]
n-$C_5H_{11}-\underset{OH}{CH}-CH_2-$	Br	H	H	+ 5°	91[c]
$C_6H_5-\underset{OH}{CH}-CH_2-$	Br	H	H	+10°	92[b]
$H_3CO-CH_2-CH_2-$	Cl	H	H	+ 5°	98[a]
	Cl	H	H	+10°	95[a]
$C_6H_5-\underset{OCH_3}{CH}-CH_2-$	Cl	H	H	+10°	97[a]
$C_6H_5-\underset{OCH_3}{CH}-CH_2$	Br	H	H	+10°	97[a]

 $R^1HgC-C(R^2)(X)-R^3$				Reaction temperature	Yield [%]
R^1	X	R^2	R^3		
 $C_6H_5-CH(OCH_3)-CH_2-$	I	H	H	+10°	95[a]
	Cl	H	H	+10°	35[a]
$O=CH-CH_2-$	Cl	H	H	+ 5°	70[b]
$O=CH-CH$ -	Cl	H	CH_3	0°	54[c]
$O=CH-CH_2-$	Cl	H	C_2H_5	- 5°	57[c]
 $H_3C-C(=O)-CH_2-$	Cl	H	H	+ 5°	95[b]
 $H_3C-C(=O)-CH_2-$	Cl	H	CH_3	0°	85[c]
 $H_3C-C(=O)-CH_2-$	Cl	H	C_2H_5	- 5°	88[c]
 $H_3C-C(=O)-CH_2-$	Cl	C_6H_5	C_6H_5	0°	36[c]
 $C_6H_5-C(=O)-CH_2-$	Cl	H	H	+ 5°	95[b]
 $C_6H_5-C(=O)-CH_2-$	Cl	H	CH_3	0°	90[c]
 $C_6H_5-C(=O)-CH(CH_3)-$	Cl	H	H	+ 5°	68[b]
$H_3COOC-CH_2-$	Cl	H	H	+ 5°	99[a]
$C_2H_5OOC-CH_2-$	Cl	H	CH_3	0°	95[b]
	Cl	H	H	+ 5°	97[a]

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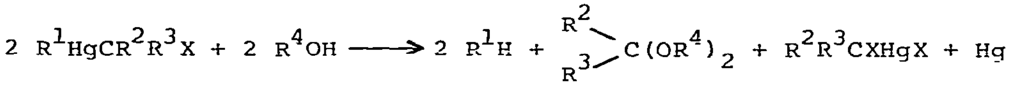
[a] Stable below - 10°.

[b] More than 50% decomposition within 1-10 days at -10°.

[c] More than 50% decomposition within less than 1 day at -10°.

Thermolysis of $R^1HgCR^2R^3X$ compounds in the presence of alcohols leads to the formation of acetals (62):



$$2\ R^1HgCR^2R^3X + 2\ R^4OH \longrightarrow 2\ R^1H + R^2R^3C(OR^4)_2 + R^2R^3CXHgX + Hg$$

The optimum reaction conditions are indicated in Table 9.

Table 9

Preparation of Acetals (Optimum Conditions)[a]

R^2	R^3	R^4	R^4	Reaction conditions	Yield [%]	
in $R^2R^3C(OR^4)_2$					Acetal	recovered Hg(0)
H	H	CH_3	CH_3	11 h, 50°	40	44
H	H	C_2H_5	C_2H_5	13 h, 50°	42	45
H	H	$i\text{-}C_4H_9$	$i\text{-}C_4H_9$	13 h, 60°	44	45
H	H	$-CH_2-C_6H_5$	$-CH_2-C_6H_5$	13 h, 80°	44	46
H	H	$i\text{-}C_3H_7$	$i\text{-}C_3H_7$	12 h, 60°	41	43
H	H	$sec\text{-}C_4H_9$	$sec\text{-}C_4H_9$	13 h, 60°	43	45
H	H	$c\text{-}C_6H_{11}$	$c\text{-}C_6H_{11}$	13 h, 60°	43	44
C_6H_5	C_6H_5	$-CH_2-CH_2-$		30 min, 20°	36	38

[a] Decomposition of $CH_3C(O)CH_2HgCR^2R^3Cl$ in presence of R^4OH.

Mercurials of type R^1HgCHR^2Cl also were found to react with four molar equivalents of an aromatic amine to give bis(4-aminophenyl)alkanes in high yield (63):

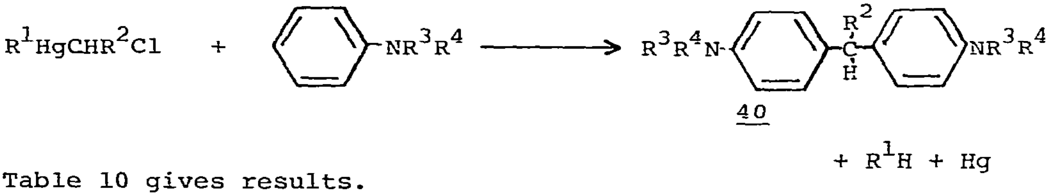


Table 10 gives results.

Table 10.

Reactions of R^1HgCHR^2Cl with Aromatic Amines (63).

R^1HgCHR^2Cl		 $-NR^3R^4$		<u>40</u>, % yield
R^1	R^2	R^3	R^4	
$HC(O)CH_2$	H	H	H	88
$MeC(O)CH_2$	H	H	H*	74
$MeC(O)CH_2$	H	Me	Me	78
$MeOC(O)CH_2$	H	H	Ph	43
$MeC(O)CH_2$	Et	Me	Me	69

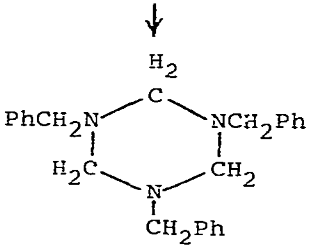
* aryl = 2,6-xylyl.

With primary or secondary aromatic amines the reactions proceeded rapidly at room temperature, but heating at 100-125°C was required for tertiary aromatic amines. The diphenyldiazomethane-derived mercurial reacted differently:

$$MeC(O)CH_2HgCPh_2Cl + PhNH_2 \longrightarrow \underset{(98\%)}{Ph_2C{=}NPh} + Me_2C{=}O + Hg$$

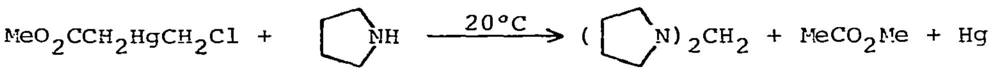
A similar reaction course appeared to be followed when primary aliphatic amines were used:

$$MeC(O)CH_2HgCH_2Cl + PhNH_2 \xrightarrow{20°C} [PhCH_2N{=}CH_2] + Me_2C{=}O + Hg$$



(55%)

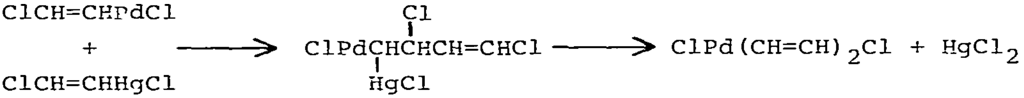
On the other hand, secondary aliphatic amines gave diaminomethanes:



Carbenes do not appear to be involved as intermediates in these reactions.

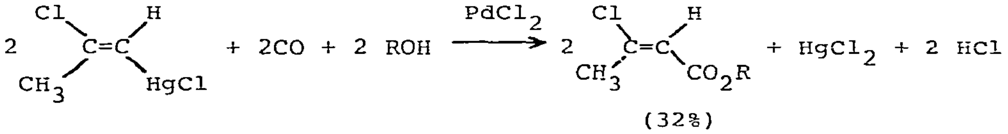
There have been more reports of transition metal-catalyzed reactions of organomercurials which can find use in organic syntheses. Many of these are catalyzed by Pd(II) complexes.

trans-β-Chlorovinylmercuric chloride was converted to a mixture of conjugated α,ω-dichloropolyenes., $Cl(CH{=}CH)_nCl$ (n = 4, 6, 8, 10, 12), with 1,4-dichloro-1,3-butadiene being the major component, by catalytic quantities of $PdCl_2$ in the presence of an oxidant such as iron (III) chloride or p-benzoquinone (64). The action of Au(III), Pt(IV) and Rh(III) chlorides and $[Rh(CO)_2Cl]_2$ on trans-ClCH=CHHgCl also gave 1,4-dichloro-1,3-butadiene. It was suggested that the higher polyenes are formed in an addition-elimination process:

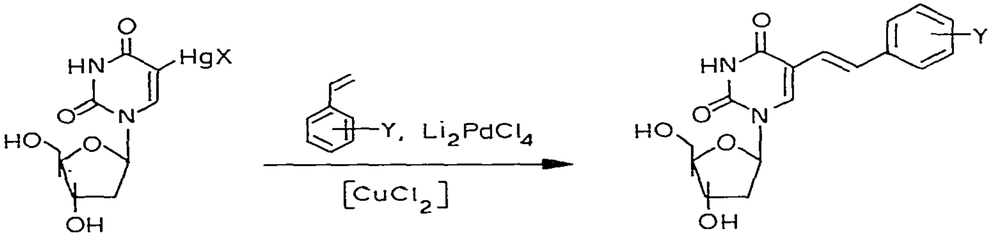


$$\begin{matrix} ClCH{=}CHPdCl \\ + \\ ClCH{=}CHHgCl \end{matrix} \longrightarrow ClPd\underset{\substack{|\\ HgCl}}{C}H\overset{\substack{Cl\\ |}}{C}HCH{=}CHCl \longrightarrow ClPd(CH{=}CH)_2Cl + HgCl_2$$

In the presence of catalytic $PdCl_2$ and stoichiometric $FeCl_3$ 1-chloromercuri-2-chloro-1-propene was carbonylated by carbon monoxide (39):



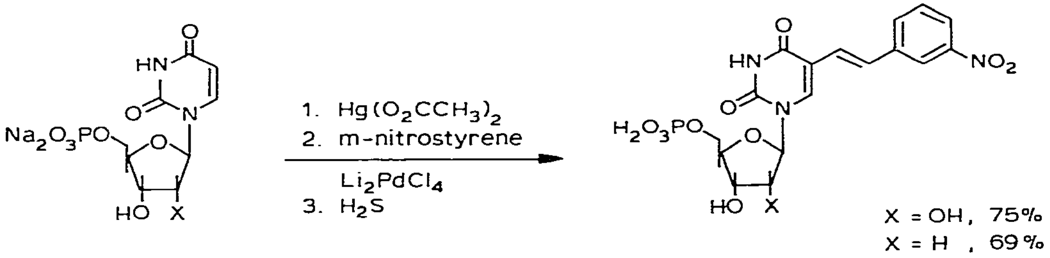
Also reported have been syntheses of 5-styryl derivatives of uracil nucleosides and nucleotides (65):



X = Cl, OAc, O_2CCF_3

Y = m-NO_2, p-NO_2, H

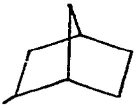
In the absence of copper(II) chloride, Li_2PdCl_4 was used as a stoichiometric reagent; when $CuCl_2$ was present as a re-oxidant, 10 mol % of Li_2PdCl_4 was used. Product yields were in the 40-55% range.



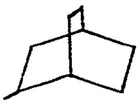
The reduction of organomercuric salts with sodium borohydride is a process which involves unstable RHgH intermediates which decompose to give free radicals. Although this procedure usually is used to convert mercurials, RHgX, to the hydrocarbons, RH, this reduction reaction can be used to carry out other kinds of free radical chemistry. In one such study, alkylmercuric halides were reduced with $NaBH_4$ in the presence of $CCl_4/CBrCl_3$ mixtures and the selectivities of the resulting alkyl radicals were determined (66):

$$\mathrm{RHgX} \xrightarrow{\mathrm{NaBH_4}} \mathrm{RHgH} \longrightarrow \mathrm{R}\cdot \xrightarrow{\mathrm{XCCl_3}} \mathrm{RX} + \mathrm{Cl_3C}\cdot \qquad (\mathrm{X = Cl,\ Br})$$

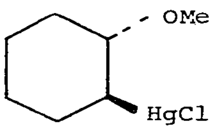
(R = CH_3, n-C_6H_{13}, n-C_8H_{17}, cyclo-C_6H_{11}, n-$C_8H_{17}CMe_2$, CH_3CEt_2,



,

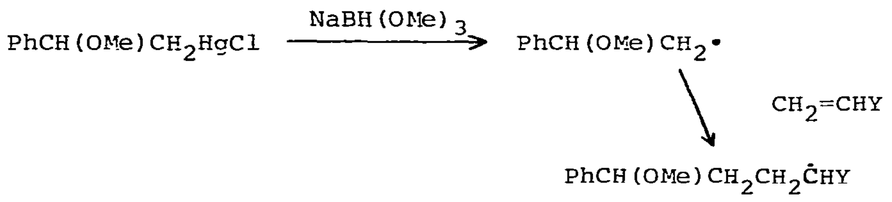


In another study, $NaBH(OMe)_3$ was used to generate the nucleophilic β-methoxyalkyl radicals from <u>41</u> and from $PhCH(OMe)CH_2HgCl$ in the

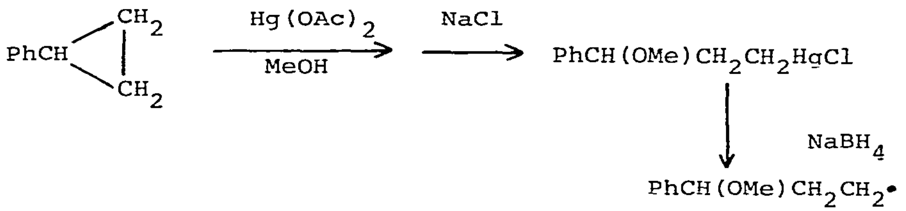


<u>41</u>

presence of suitable electrophilic olefins (e.g., acrylonitrile, methyl acrylate, styrene, etc.) (67):

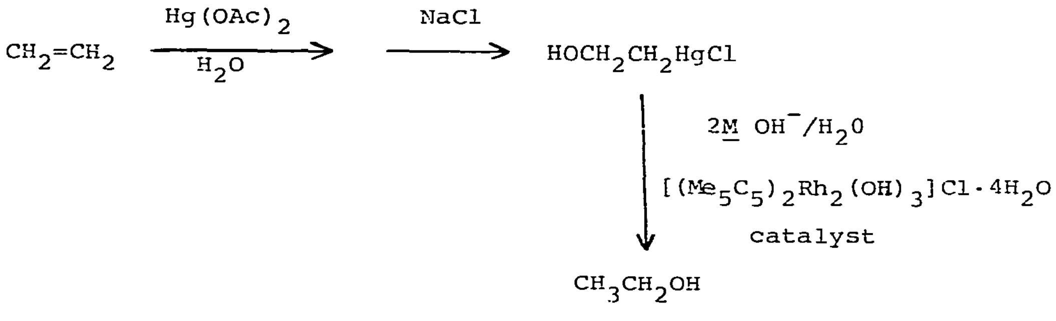


Hydrogen transfer from the PhCH(OMe)CH_2HgH intermediate then gives the final product, PhCH(OMe)$CH_2CH_2CH_2$Y. Cyclopropane methoxymercuration products, i.e., γ-methoxyalkylmercurials, provided γ-methoxyalkyl radicals (68):



These radicals also were trapped with electrophilic olefins.

A catalytic RHgX-to-RH conversion was the basis for a new ethylene → ethanol process (69):



The yields, however, were poor: 0.12-0.15 equivalent of ethanol per equivalent of the mercurial. Some acetaldehyde and much acetate were formed as well. In an analogous reaction, propylene gave some isopropanol.

Mercury(II) carboxylates react with aliphatic iodides in THF to give esters (70). Some solvent involvement occurs:

$$(RCO_2)_2Hg + R'I \longrightarrow RCO_2R' + RCO_2(CH_2)_4OR'$$

Some results are given below:

R in $(RCO_2)_2Hg$	R' in R'I	RCO_2R'	$RCO_2(CH_2)_4OR'$
CH_3	Et	25%	30%
O_2NCF_2	Me	9%	31%
$2,4,6\text{-}Cl_3C_6H_2OCH_2$	Et	not detnd.	33%
$2,4,6\text{-}Cl_3C_6H_2OCH_2$	n-Bu	not detnd.	42%
CF_3	Et	not detnd.	40%
CF_3	n-Bu	not detnd.	42%

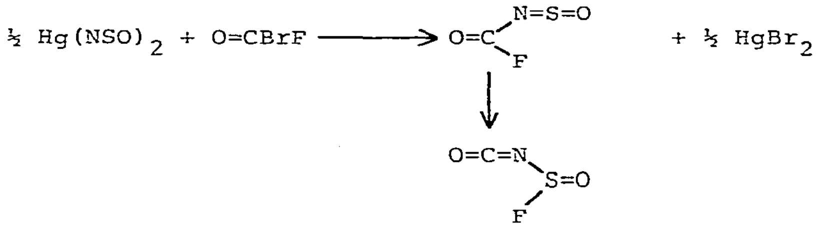
Other workers have used the reactions of mercury(I) carboxylates with bromine to prepare organic bromides (71):

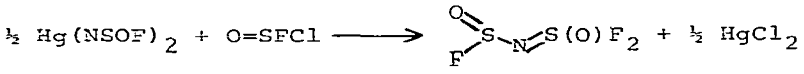
$$RCO_2Hg\text{-}HgO_2CR + Br_2 \longrightarrow 2\ RBr + 2\ CO_2 + 2\ HgBr_2$$

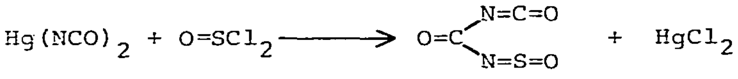
On the other hand, the reaction of iodine with mercury(I) carboxylates resulted in formation of esters, with only limited amounts of organic iodides being produced:

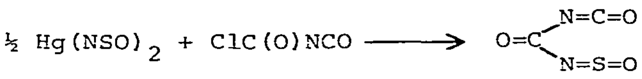
$$RCO_2Hg\text{-}HgO_2CR + 2\ I_2 \longrightarrow RCO_2R + CO_2 + 2\ HgI_2$$

Novel products were obtained in some reactions of mercury-nitrogen compounds with halides (72, 73):





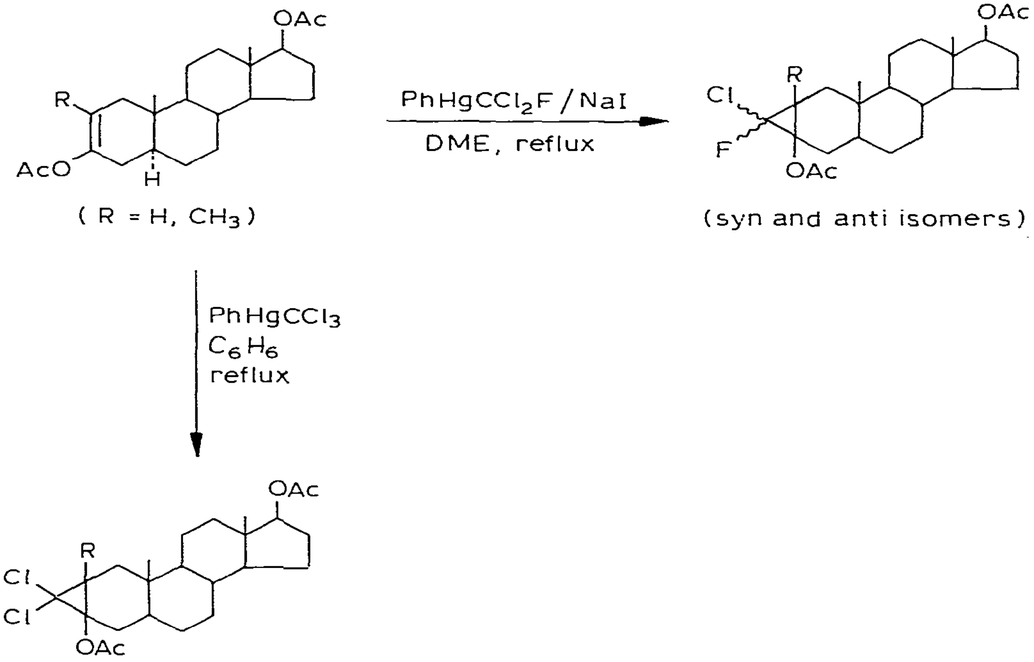




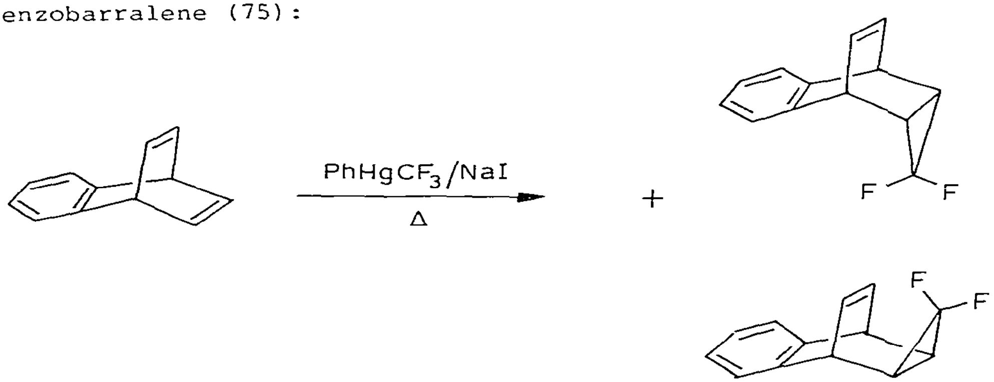
$$Hg(NSOF_2)_2 + CX_4 \longrightarrow F_nC(NSOF_2)_{4-n}$$

Some new examples of the use of phenyl(trihalomethyl)mercury compounds in the synthesis of gem-dihalocyclopropanes have been reported:

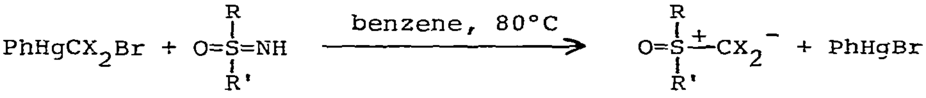
Steroidal Olefins (74):



Benzobarralene (75):



Phenyl(trihalomethyl)mercurials were found to react with sulfoximes to give oxosulfonium ylides as the major product (76):

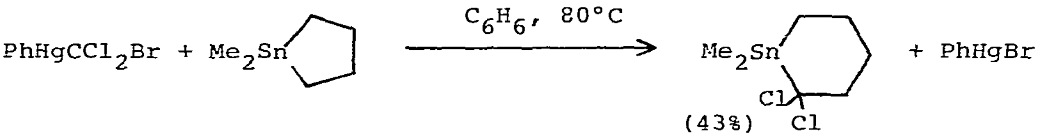


$$\mathrm{PhHgCX_2Br} + \mathrm{O{=}\overset{R}{\underset{R'}{S}}{=}NH} \xrightarrow{\text{benzene, 80°C}} \mathrm{O{=}\overset{R}{\underset{R'}{S}}\overset{+}{-}CX_2^{-}} + \mathrm{PhHgBr}$$

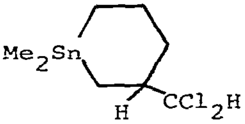
(X = Cl, Br) (R, R' = Ph, Ph
Me, Me
Me, Ph)

The corresponding sulfoxide, RS(O)R', and tetrahaloethylene, $CX_2{=}CX_2$, were formed as minor by-products. Although the mechanism of this reaction was not established by experiment, the rapid rate of the reaction suggested a bimolecular, non-carbene process.

Also of interest is the insertion of $PhHgCCl_2Br$-derived dichlorocarbene into the strained stannacyclopentane ring (77):



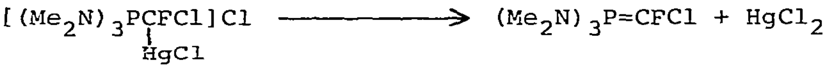
In contrast, the unstrained 1,1-dimethyl-1-stannacyclohexane reacted with $PhHgCCl_2Br$ to give the β C-H insertion product, 42 (Seyferth and Washburne, 1966).



42

The novel organomercury reagent $[(Me_2N)_3PCFClHgCl]^+Cl^-$ has been prepared and has been demonstrated to be an effective 1-chloro-1-fluorovinylation reagent (78):

$$[(Me_2N)_3PCFCl_2]Cl + Hg \xrightarrow{60°C} [(Me_2N)_3PCFClHgCl]Cl$$



$$[(Me_2N)_3P\underset{HgCl}{C}FCl]Cl \longrightarrow (Me_2N)_3P{=}CFCl + HgCl_2$$

$$(Me_2N)_3P{=}CFCl + R_2C{=}O \longrightarrow R_2C{=}CFCl + (Me_2N)_3PO$$

In practice, this chemistry may be carried out in the "one-pot" manner or stepwise. In one example, $[(Me_2N)_3PCFClHgCl]Cl$ was prepared in benzonitrile (83 hr. at 60°C); subsequent reaction with benzaldehyde gave PhCH=CFCl (a nearly 1:1 mixture of E and Z isomers) in 73% yield. The zinc-containing phosphonium salt, prepared in the same manner, reacted with mercury(II) halides:

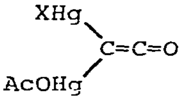
$$[(Me_2N)_3PCFClZnCl]Cl + RHgCl \longrightarrow \underset{\underline{43}}{[(Me_2N)_3PCFClHgR]ZnCl_3}$$

$$(R = Cl,\ Ph)$$

Products of type 43 were chlorofluoro-olefination reagents only in the presence of external iodide ion. Apparently, it is halide ion attack at mercury in the cations which generates $(Me_2N)_3P{=}CFCl$.

5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS.

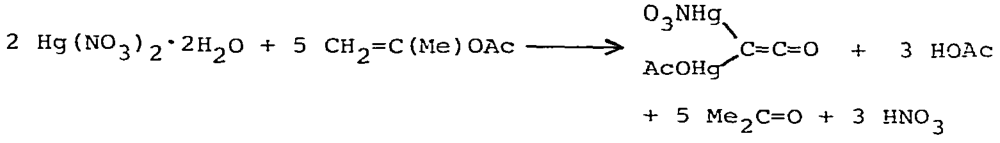
Of special interest are organomercury(I) and -(II) ketenide derivatives reported by Blues et al. (79). The former are the first stable organomercury(I) compounds to be characterized. The Hg(II) ketenides can be prepared by heating mercuric acetate, nitrate or perchlorate with acetic anhydride at 60°C in acetonitrile solution. They are isolated in the form of insoluble white solids in 60-80% yield. Although represented as 44, they obviously are associated.



$(XHg)(AcOHg)C{=}C{=}O$ $(X = OAc,\ NO_3,\ ClO_4)$

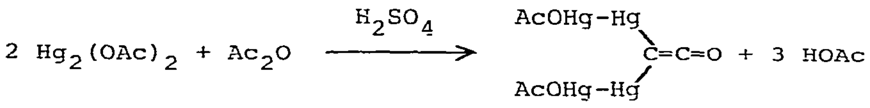
44

Another preparation is based on isopropenyl acetate:



$$2\ Hg(NO_3)_2 \cdot 2H_2O + 5\ CH_2{=}C(Me)OAc \longrightarrow (O_3NHg)(AcOHg)C{=}C{=}O + 3\ HOAc + 5\ Me_2C{=}O + 3\ HNO_3$$

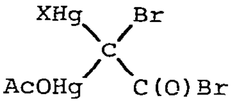
The Hg(I) ketenides were prepared similarly:



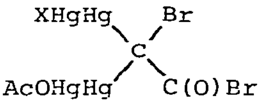
$$2\ Hg_2(OAc)_2 + Ac_2O \xrightarrow{H_2SO_4} (AcOHg{-}Hg)_2C{=}C{=}O + 3\ HOAc$$

45

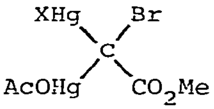
They also were insoluble in organic solvents and probably associated. Both types of ketenides are stable at room temperature in dry air; rapid thermolysis gave carbon suboxide. Both react with gaseous HCl to give $CH_2{=}C{=}O$ and acetyl chloride. Bromination resulted in 46 and 47. Acid bromide 46 gave ester 48 on treatment



46



47



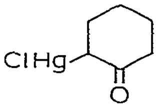
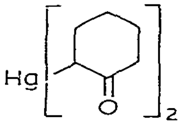
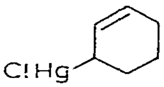
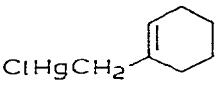
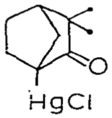
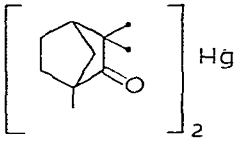
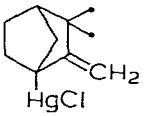
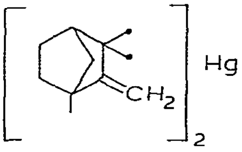
48

with methanol, and sodium borohydride reduction of 48 produced methyl bromoacetate. The main evidence for the constitution of 45 as a mercurous compound was provided by its hydrolysis in dilute aqueous HCl to give, in quantitative yield, mercurous chloride as the sole mercury-containing product, and acetic acid as the only organic product.

Nesmeyanov et al. (80) have reported detailed physical and spectroscopic studies (^{13}C NMR and Raman spectra, half-wave reduction potentials and mass spectra) for groups of organomercurials

TABLE 11.

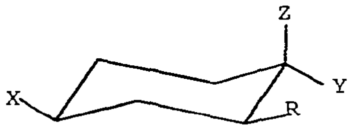
Compounds Studied in σ,π-Bonding Investigation (80).

A	B
$ClHgCH_2CHO$ $ClHgCH_2COC_2H_5$  $Hg(CH_2CHO)_2$ $Hg(CH_2COC_2H_5)_2$ $Hg(CH_2COC_6H_5)_2$  $ClHgCH_2CH{=}CH_2$   $Hg(CH_2CH{=}CH_2)_2$	   

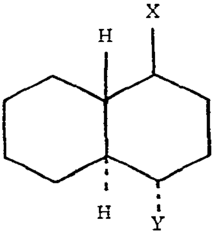
containing carbonyl and allyl functionality in which σ,π-conjugation (i.e., interaction of the C-Hg σ-bond with a π-system) is possible (Group A in Table 11) and in which it is not (Group B in Table 11). The evidence obtained in favor of σ,π-conjugation was decisive.

Table 12

Cyclohexyl Sulfonates Studied (81)

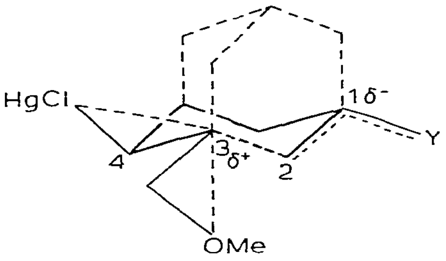


X	Y‡	Z	R
HgCl	OBs	H	Me
H	OBs	H	Me
HgCl	ONs	H	$CH_2-CH_2-CH=CH_2$
H	ONs	H	$CH_2-CH_2-CH=CH_2$
HgCl	OTs	H	H
HgCl	H	OTs	H
H	OTs	H	H



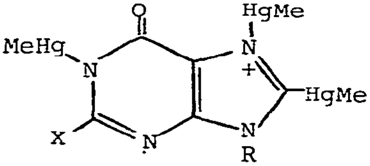
X	Y‡
HgCl	OTs
H	OTs

‡Bs = p-bromophenylsulphonyl
Ns = p-nitrophenylsulphonyl
Ts = p-tolylsulphonyl



Hyperconjugative interaction of a ClHg substituent with a carbonium ion center, as shown in 49, was indicated by a comparison of the solvolysis of the pairs of cyclohexyl sulfonates shown in Table 12. The presence of the ClHg group was found to lead to an increased substitution/elimination ratio and to extensive retention of configuration, but had little influence on the solvolysis rate (81).

C-Mercurated products, 50, were obtained when ionosine and guanosine were treated with methylmercuric nitrate at pH 7-8 (82).



50 (X = H(ionosine), NH$_2$(guanosine);
R = ribose)

The formation of these products was suggested to occur *via* the reaction course shown below:

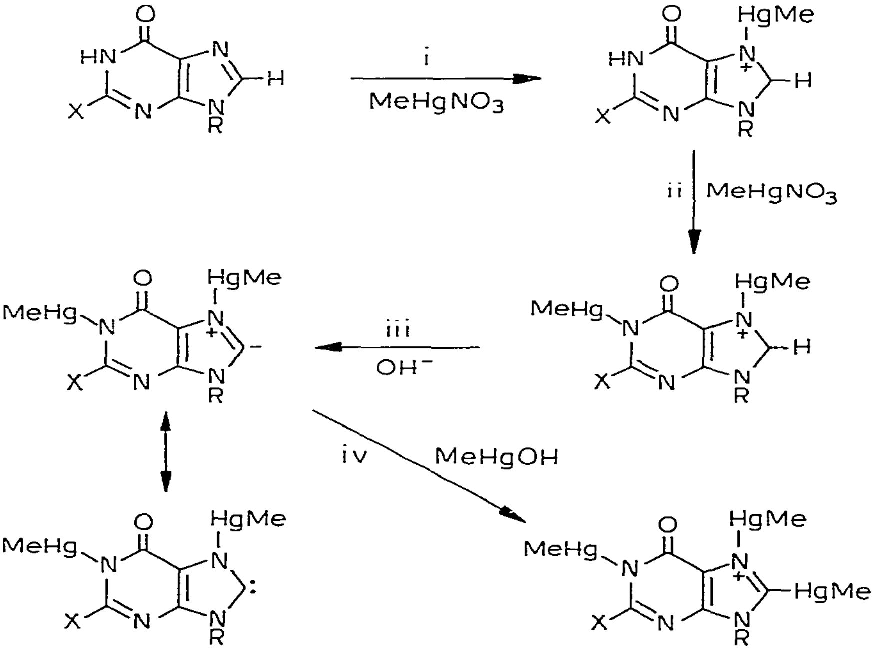
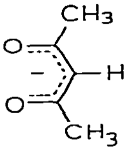
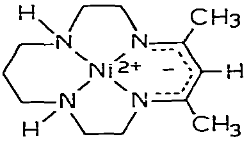
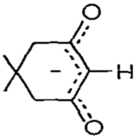
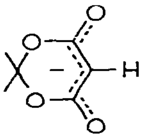
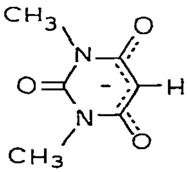
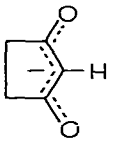


Table 12a.
Stability Constants of the Methylmercury-Carbon Donor Complexes

protonated ligand	conjugate base (L)	pK_a	$\log K_{CH_3HgL}{}^a$
malononitrile	$CH(CN)_2^-$	11.39	10.40 8.52
acetylacetone		9.0 $(8.24)_{enol}$	5.9
$[Ni([14]dieneN_4)]^{2+}$		6.28	5.46
dimedone		5.25 $(5.23)_{enol}$	3.70
Meldrum's acid		4.83 $(2.48)_{enol}$	3.72
1,3-dimethylbarbituric acid		4.45	3.60
1,3-cyclopentanedione		4.25	2.1

$^a\log K_{CH_3HgL} = \log([CH_3HgL/[CH_3Hg][L]); I = 0.10(NaClO_4)$; 20°C.

A linear correlation between ligand pK_a and the methylmercury stability constant ($\log K_{CH_3HgL} = 0.8pK_a$) has been established for a series of functional carbon-donor ligands (82a). Because the ligands were so diverse (Table 12A), the correlation is not as well defined as in the case of P-, S-, N- and O-donor ligands studied previously. In aqueous solution, $CH_3Hg(II)$ transfer reactions can be more than four orders of magnitude faster than proton transfer reactions [due to the superior bridging ability of $CH_3Hg(II)$], but protonation is thermodynamically preferred. It is of interest that the Raman frequencies of the symmetric CH_3-Hg vibration in $CH_3Hg(II)$ complexes may be used to differentiate between Hg-C (540-565 cm^{-1}) and Hg-O (565-580 cm^{-1}) bonding.

6. MERCURY-CARBON BOND REACTIONS

Reactions of organomercurials in which Hg-C bonds are broken, redistributed or formed have long been of interest to physical organic chemists and much work has been done in the area of mechanistic organomercury chemistry. In this year's survey we note several papers from the laboratories of some leading contributors to this area, O. A. Reutov and F. R. Jensen.

More detailed examination of the one-bromide ion-catalyzed bromine cleavage of alkylmercuric bromides, an S_E2 process, has revealed that the rates of such reactions are subject to both large rate-retarding steric effects (maximum effect in β-branched alkyl substituents) and large opposing rate-accelerating electronic effects (maximum effect in α-branched alkyl groups) (83). Table 13 shows relevant rate constants for reactions of type:

$$RHgBr + Br_2 \xrightarrow[\text{MeOH}]{\text{large excess } Br^-} RBr + HgBr_2$$

When R = primary alkyl, the correlation $k_R/k_{Me} = -10.9\ \sigma^* + 1.5\ E_S$ was found to be applicable. When R = secondary alkyl, $k_R/k_{Me} = -17.9\ \sigma^* + 1.054E_S$ (σ^* = Taft inductive parameter; E_S = Taft steric factor). These reactions proceeded with retention of configuration.

Reutov and his coworkers have shown that the solvent has a considerable effect on redistribution equilibria in organomercury chemistry. In a new investigation (84), Reutov et al. have found that the K_{eq} for the reaction:

$$(MeO_2CCH_2)_2Hg + Hg(CN)_2 \overset{K\ eq}{\rightleftharpoons} 2\ MeO_2CCH_2HgCN$$

in dry N,N-dimethylformamide in the presence of 0.1M $Bu_4N^+ClO_4^-$ also is greatly dependent on the dielectric constant of the solvent system used (Table 14). Thus the higher the dielectric constant of the medium, the more favorable is the formation of the unsymmetrical species. The redistribution reaction below has been

$$R_2Hg + HgCl_2 \overset{DMF}{\rightleftharpoons} 2\ RHgCl$$

(R = Et, Ph, Vi, $PhCH_2$, C_6F_5, MeO_2CCH_2, $(CF_3)_2CH$, $CH_3C(O)CH_2$)

studied in detail using polarography and potentiometric titration (85). The relative rates in the absence of added chloride ion decreased in the order: Ph ~ Vi > Et > $PhCH_2$ > C_6F_5 > $MeOCCH_2$ >> $(CF_3)_2CH$. In all cases, with the exception of $[CH_3C(O)CH_2]_2Hg$, an S_E2-type mechanism obtained. Chloride ion was found to have a rate-retarding effect for all mercurials studied except $(C_6F_5)_2Hg$. In the case of the latter, chloride ion had a large rate-accelerating effect. It was suggested that this was due either to the

Table 13.

Pseudo-Third-Order Rate Constants for the One-Bromide Ion-Catalyzed Bromine Cleavage of Alkylmercuric Bromides in Methanol at 25.0°C at 0.30 M Ionic Strength (83).

	RHgBr,R	$k_{3A}K_2$ or $k_{3B}K_1$, s^{-1} M^{-2}
α branching	methyl	1.68
	ethyl	18.1
	isopropyl	1310
	tert-butyl	5660
β branching (primary R)	ethyl	18.1
	n-propyl	7.43
	isobutyl	2.09
	neopentyl	0.2903
β branching (secondary R	isopropyl	1310
	sec-butyl	1016
	$Me_2CHCH(Me)$-	
	$Me_3CCH(Me)$-	53.3
γ branching (primary R)	n-propyl	7.43
	n-butyl	8.32
	$Me_2CHCH_2CH_2$-	
	$Me_3CCH_2CH_2$-	12.5

Table 14.

Effect of Medium on the Equilibrium in the $(MeO_2CCH_2)_2Hg + Hg(CN)_2$ Redistribution (84)

Medium	Dielectric Constant	Keq
Pyridine	12.4	0.004
80% Pyridine + 20% DMSO	19.4	0.058
60% Pyridine + 40% DMSO	26.1	0.16
40% Pyridine + 60% DMSO	33.0	1.17
DMSO	46.7	2.54

operation of nucleophilic one-anion catalysis or to the intervention of an $S_E2(R^-M^+)$ mechanism.

Mechanisms of the reactions of organomercurials with organic halides have been studied by Russian workers at Gorkii. The reaction of phenylmercuric bromide with bromobenzene (photochemically or thermally induced) gives mercuric bromide and biphenyl as products. When ^{14}C-labeled bromobenzene was used, there was slight C_6H_5 group exchange between PhHgBr and PhBr as indicated by introduction of small amounts of ^{14}C label into the phenylmercuric bromide in reactions not carried out to completion. The biphenyl, however, contained 40% of the activity of the original labeled bromobenzene. A radical mechanism is indicated (86):

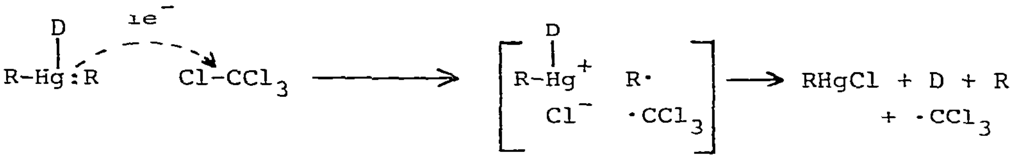
$$C_6H_5HgBr \xrightarrow{h\nu \text{ or } \Delta} C_6H_5\cdot + BrHg\cdot$$

$$^{14}C_6H_5Br + \cdot HgBr \longrightarrow HgBr_2 + {}^{14}C_6H_5\cdot$$

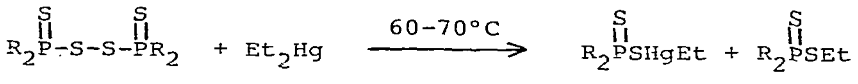
$$^{14}C_6H_5\cdot + C_6H_5HgBr \longrightarrow {}^{14}C_6H_5HgBr + C_6H_5\cdot$$

$$C_6H_5\cdot + {}^{14}C_6H_5\cdot \longrightarrow {}^{14}C_6H_5\text{-}C_6H_5$$

Substantial phenyl group exchange between PhHgBr and PhBr occurred in the photochemical and thermal reactions when cobalt(II) chloride or metallic silver were present, and these additives also increased the reaction rates. Presumably, organometallic intermediates, PhCoCl and PhAg, are involved. An investigation of the effect of donor molecules such as dioxane, pyridine, THF and HMPA on the reaction of dialkylmercurials with polychloromethanes showed that these Lewis bases accelerate the reactions (87). It was proposed that complex formation between the dialkylmercury compound and the Lewis base is followed by reaction of the complex with the polychloromethane by an electron-transfer mechanism:



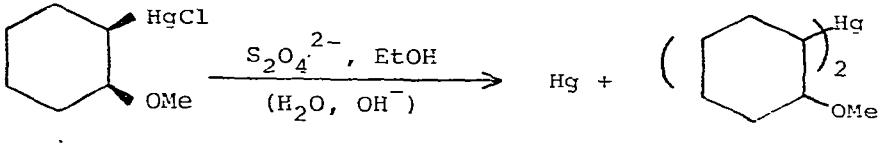
Another reaction which quite likely involves a radical process is that of diethylmercury with phosphorus-containing disulfides (88):



$$R_2\overset{S}{\overset{\|}{P}}\text{-S-S-}\overset{S}{\overset{\|}{P}}R_2 + Et_2Hg \xrightarrow{60\text{-}70°C} R_2\overset{S}{\overset{\|}{P}}SHgEt + R_2\overset{S}{\overset{\|}{P}}SEt$$

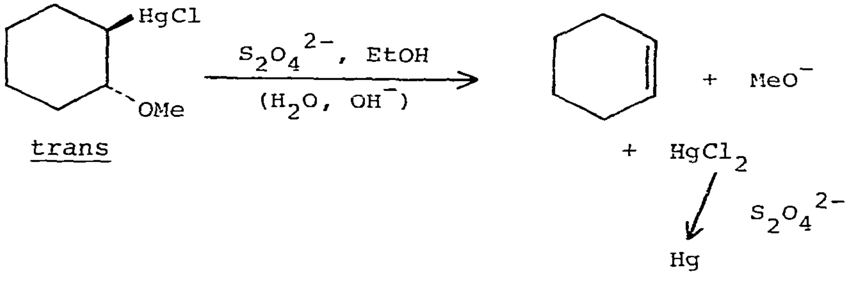
(R = Ar, R'O)

The reaction course observed when organomercuric halides are treated with sodium dithionite depends on the group R in RHgX (89). Alkylmercuric salts undergo one-electron reduction with this reagent. Optically active sec-butylmercuric salts were converted to racemic di-sec-butylmercury. Olefin oxymercuration products were converted to the symmetrical mercurials or underwent reversion to olefin and Hg(II) salt in the presence of $S_2O_4^{2-}$, depending on their structures:



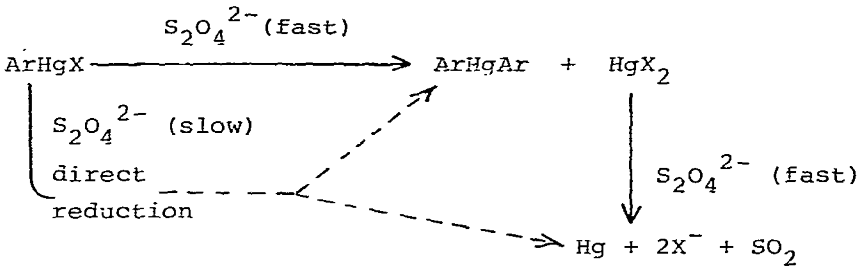
cis

(with racemization)

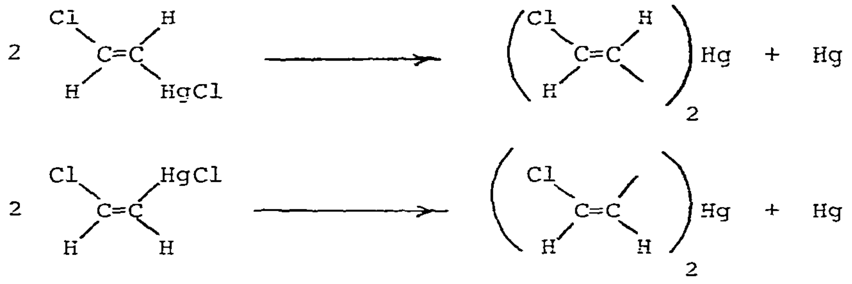


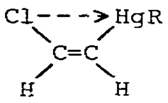
trans

Arylmercuric salts are readily symmetrized by $S_2O_4^{2-}$ and the Hg(II) salt formed is reduced:



Electrochemical reduction of organomercurials also has received further attention. The cis and trans isomers of ClCH=CHHgCl and $(ClCH=CH)_2Hg$ were reduced polarographically in dry acetonitrile (90). In the case of the former, the reductive symmetrization occurred with retention of configuration. The fact that the cis isomers are reduced at lower potentials that the trans isomers, i.e., with greater facility, was interpreted as providing evidence for intramolecular Cl→Hg coordination in the cis isomer:



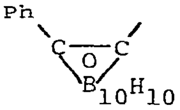


Butin, Ismail and Reutov (91) have utilized the rotating disk-ring electrode of Frumkin and Nekrasov in the generation and electrochemical oxidation of carbanions derived from diorganomercurials, R_2Hg (R = CN, $CF(NO_2)_2$, C_6H_5, C≡CPh, $C{\equiv}COC_6H_4NO_2$-p, $C{\equiv}CCH_2S$-Ph, $CH_2C(O)Ph$, CH_2CN, $Cl{=}CCl_2$, 2-Ph-o-carboranyl):

$$R_2Hg + 2e^- \xrightarrow[CH_3CN]{\text{Pt disk}} 2R^- + Hg$$

Table 15.

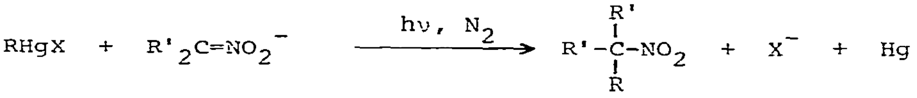
Reduction Potentials of R_2Hg* (91)

R in R_2Hg	$E_{\frac{1}{2}}$, V (vs. S.C.E.)
$CF(NO_2)_2$	+ 0.05
$CH_2C(O)Ph$	- 1.05
CH_2CN	- 0.62
CN	- 0.45
$C{\equiv}COC_6H_4NO_2$-p	- 1.08
$C{\equiv}CCH_2SPh$	- 1.14
$C{\equiv}CPh$	- 1.42
$CCl{=}CCl_2$	- 1.33
C_6F_5	- 1.26
	- 1.00

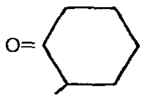
*In the presence of 0.05M n-$Bu_4N^+BF_4^-$ in acetonitrile at 25°C, platinum disk.

Reduction potentials are listed in Table 15.

Primary or secondary alkylmercuric halides have been found to react with nitronate anions in DMSO or DMF *via* a free-radical nucleophilic substitution ($S_{RN}1$) process (92):



$$RHgX + R'_2C{=}NO_2^- \xrightarrow{h\nu,\ N_2} R'-\overset{\displaystyle R'}{\underset{\displaystyle R}{C}}-NO_2 + X^- + Hg$$

(R = $PhCH_2$, n-C_6H_{13}, cyclo-C_6H_{11}, )

UV irradiation is necessary and these reactions are inhibited by 5 mol % of di-t-butylnitroxide. Such reactions were not observed with phenyl- or vinylmercuric halides.

Photolysis of cyclopentadienylmercurials, $(CH_3C_5H_4)_2Hg$,

$(Me_3CC_5H_4)_2Hg$ and $(Me_3SiC_5H_4)_2Hg$, yielded the respective cyclopentadienyl radicals, whose ESR spectra were measured (93). Thermolysis of ten substituted dibenzylmercurials has been used to generate benzyl radicals and to derive a scale of substituent constants for the para-substituted mercurials (whose derived benzyl radicals are resonance-stabilized) (94). Table 16 presents rate constants and derived substituent constants.

Finally, we note some insertions into mercury-carbon bonds. Dibenzylmercury compounds, $(RC_6H_4CH_2)_2Hg$, reacted quantitatively with tetracyanoethylene to give $RC_6H_4CH_2C(CN)_2C(CN)_2HgCH_2C_6H_4R$, with the rate of insertion increasing in the order $p\text{-}CF_3 \ll H < p\text{-}CH_3$ (95). In such reactions, an initial dark blue charge-transfer complex is formed in dichloromethane solution at 30°C. The prod-

Table 16.

Rate constants for the decomposition of $(XC_6H_4CH_2)_2Hg$ at 140.2°C in octane.[a]

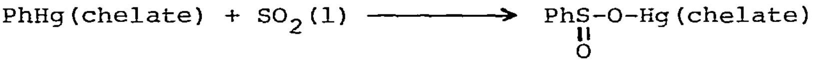
X	$10^5 \times k_1 (s^{-1})$	$\sigma \cdot$[b]
H	8·1	0
m-F	5·6	
m-OMe	7·3	
3,5-Me_2	11·3	
p-Cl	7·2	0·06
p-F	9·4	0·07
p-OMe	26·3	0·31
p-Me	26·6	0·38
p-Ph	21·7	0·39
p-NO_2	15·6	0·73

[a] Decompositions are kinetically of first order; the rate-determining step involves homolytic fission of one of the C-Hg bonds:

$$(XC_6H_4CH_2)_2Hg \longrightarrow XC_6H_4CH_2\cdot \quad + \quad XC_6H_4CH_2Hg\cdot$$

[b] For application in the equation: $\log k/k_o = \rho\sigma + \rho\cdot\sigma\cdot \quad (\rho\cdot = 1)$

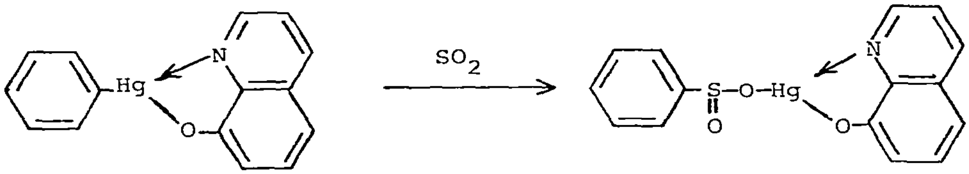
ucts are isolated as pale yellow solids. These decompose in solution at room temperature to give the benzylmercuric cyanide. Sulfur dioxide insertions into the Hg–Ph bond of a number of phenylmercury chelate compounds have been reported by an Indian group (96):



$$\text{PhHg(chelate)} + SO_2(l) \longrightarrow \text{Ph}\underset{\overset{\|}{O}}{S}\text{–O–Hg(chelate)}$$

(chelate = anions derived from salicylaldehyde, 8-hydroxyquinoline, benzoyl phenylhydroxylamine, substituted benzophenones, Schiff bases)

IR studies showed the products to be O-sulfinates, e.g.:



7. MERCURY-FUNCTIONAL MERCURIALS.

A. Mercurials with Halogen and Oxy Substituents

The preparations of $Hg(SbF_6)_2$, $HgF(SbF_6)\cdot SO_2$, $HgF(BF_4)$ and $HgF(AsF_6)$ have been described (41). All are excellent sources of Hg^{2+} in liquid SO_2. All of the halides of type $C(HgX)_4$ (X = F, Cl, Br, I) have been prepared and studied by Breitinger et al. (97):

$$C(HgOAc)_4 \xrightarrow{KHF_2,\ 1M\ HOAc} \xrightarrow{40\%\ HF} C(HgF)_4$$

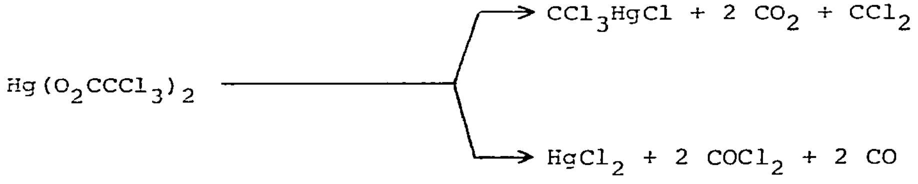
$$C(HgOAc)_4 \xrightarrow{NaX,\ 1M\ HOAc} C(HgX)_4 \quad (X = Cl, Br, I)$$

The $C(HgX)_4$ compounds are insoluble in common organic solvents, but $C(HgCl)_4$ and $C(HgBr)_4$ dissolve in DMSO. They are thermally stable to 350-400°C. $C(HgI)_4$ is yellow in color and is converted to HgI_2 by a focused laser beam. $C(HgCl)_4$ forms a water-soluble complex with thiosulfate ion.

Mercury(II) trichloroacetate has been prepared and its chemistry has been studied in detail (98):

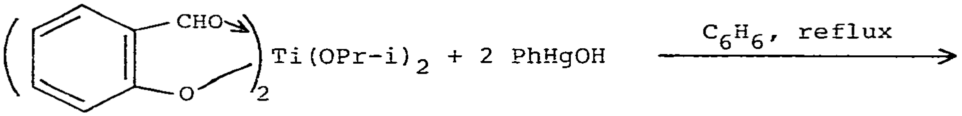
$$Hg(O_2CC_3H_7\text{-}n)_2 + 2\ CCl_3CO_2H \xrightarrow{CH_2Cl_2} Hg(O_2CCCl_3)_2 + 2\ n\text{-}C_3H_7CO_2H$$

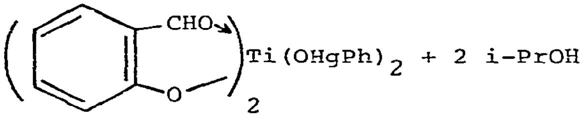
This compound is decomposed by atmospheric moisture as well as by bulk water to give mercury(I) chloride. It forms stable 1:2 complexes with pyridine and 1,10-phenanthroline. Its thermal decomposition in refluxing 1,2-dimethoxyethane gave CCl_3HgCl in 34-38% yield, in addition to $HgCl_2$, Hg_2Cl_2, CO_2, some CO and phosgene. Two decomposition pathways were suggested:



Detectable amounts of 7,7-dichloronorcarane were formed when the decomposition was carried out in cyclohexene. Benzene is mercurated smoothly by mercuric trichloroacetate. The resulting $PhHgO_2CCCl_3$ decomposes thermally to give PhHgCl; $PhHgCCl_3$ was not observed.

NMR spectroscopy was used to study aryloxy group exchange between organomercuric phenoxides and organotin and organolead phenoxides, as well as between organomercuric phenoxides and phenols (99). The systems $PhHgOAr/R_3MOAr$, with $R_3M = Et_3Sn$, Ph_3Sn and Ph_3Pb, and Ar = 4-Br-2,6-$Me_2C_6H_2$, 4-Br-2-MeC_6H_3, 2,4-Br_2-6-MeC_6H_2 and 4-O_2N-2,6-$Me_2C_6H_2$, and PhHgOAr/ArOH were examined. All exchanges were rapid on the NMR time scale in pyridine solution at 34°C, with the exception of that between PhHgOAr and Ph_3SnOAr when Ar = 2,4-Br_2-6-MeC_6H_2. The phenylmercuric phenoxides were prepared by reaction of phenylmercuric hydroxide with the appropriate substituted phenol in anhydrous methanol. The reactions of phenylmercuric hydroxide with salicyclaldehyde, 8-hydroxyquinoline, benzoylphenylhydroxylamine, 2-hydroxybenzophenone and some Schiff bases were used to prepare a number of phenylmercury chelates (100). Similar reactions of phenylmercuric hydroxide with chelated titanium isopropoxides gave stable phenylmercury titanoxanes (100):





$Ti(OHgPh)_2$ + 2 i-PrOH

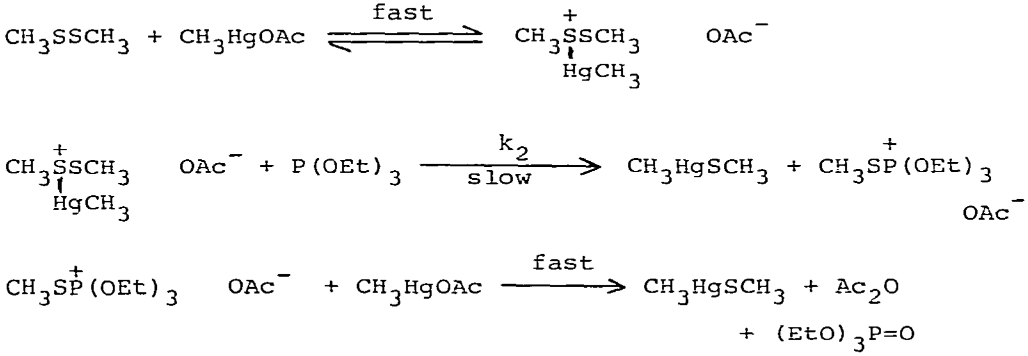
$(PhHgO)_4Ti$ also was obtained as a white solid from the reaction of PhHgOH with tetraisopropyl titanate.

B. Mercurials with Sulfur and Selenium Substituents

Russian workers have studied the CF_3CO_2H-catalyzed exchange reactions between PhHg derivatives of thiophenols and Group IV derivatives of thiophenols in chloroform solution using proton NMR spectroscopy (101). Equilibrium constants were determined for the following systems:

PhHgSPh + $Ph_3CSC_6H_4Me$-2	K_{eq} = 4.5
$PhHgSC_6H_4NMe_2$-4 + $Ph_3CSC_6H_4Me$-2	4.9
$PhHgSC_6H_4Cl$-2 + $Ph_3CSC_6H_4Me$-2	0.3
PhHgSPh + $Ph_3CSC_6H_3Me_2$-2,6	70
PhHgSPh + $Ph_3GeSC_6H_4Me$-2	4.6
PhHgSPh + $Ph_3SnSC_6H_4Me$-2	1.0
$PhHgSC_6H_4Cl$-2 + $Ph_3SnSC_6H_4Me$-2	0.27

The kinetics of the cleavage of dimethyl disulfide by methylmercuric acetate in the presence of triethyl phosphite, a reaction which gives CH_3HgSCH_3, have been studied by Bach and Rajan (102). The following mechanism was proposed:



$$CH_3SSCH_3 + CH_3HgOAc \underset{}{\overset{\text{fast}}{\rightleftharpoons}} CH_3\underset{\underset{HgCH_3}{\uparrow}}{\overset{+}{S}}SCH_3 \quad OAc^-$$

$$CH_3\underset{\underset{HgCH_3}{\uparrow}}{\overset{+}{S}}SCH_3 \quad OAc^- + P(OEt)_3 \xrightarrow[\text{slow}]{k_2} CH_3HgSCH_3 + CH_3S\overset{+}{P}(OEt)_3 \quad OAc^-$$

$$CH_3S\overset{+}{P}(OEt)_3 \quad OAc^- + CH_3HgOAc \xrightarrow{\text{fast}} CH_3HgSCH_3 + Ac_2O + (EtO)_3P{=}O$$

It is noteworthy that mercurials such as CH_3HgOAc, CH_3HgI and CH_3HgNO_3 do not cleave the S-S bond in the absence of a nucleophile.

Lippard et al. have reported very interesting studies on the use of $C(HgOAc)_4$ as a reagent for labeling sulfur in nucleic acids (103). Binding of this mercurial occurs to the sulfur atom of 6-thioguanosine and the 4-thicuridine residue of Escherichia coli $tRNA^{Val}$. Tetrakis(acetoxymercuri)methane also has been used to label fd bacteriophage; this allowed visualization of the bacteriophage in the scanning transmission electron microscope (104). Visualization occurs as bright spots which are believed to result from chemical clustering of the reagent, i.e., formation of thiolate-bridged oligomers of type

$[(RSHg)_3C\text{-}Hg\text{-}S(R)\text{-}Hg\text{-}C(HgSR)_3]$ (R = 2-aminoethyl moiety)

Tetrakis(acetoxymercuri)methane also has been found to bind to sulfur in hemoglobin (105). The tetrafunctionality of $C(HgOAc)_4$ can cause problems. This difficulty can be dealt with by treating the tetra-mercurial with three equivalents of $Me_2NCH_2CH_2SH\cdot HCl$. An essentially monofunctional sulfur-binding reagent results (103).

The compounds $Hg(SCF_3)_2$ and $Hg(SeCF_3)_2$ have found useful application as synthetic reagents:

$$(CF_3Y)_2Hg + I_nSiH_{4-n} \xrightarrow[\text{(ref. 106)}]{} (CF_3Y)_nSiH_{4-n}$$

(Y = S, Se) (n = 1-4)

$$(CF_3Y)_2Hg + IGeH_3 \xrightarrow[\text{(ref. 107)}]{} CF_3YGeH_3$$

(Y = S, Se)

$$(CF_3Y)_2Hg + IGe_2H_5 \xrightarrow[\text{(ref. 107)}]{} CF_3YGe_2H_5$$

$$(CF_3Y)_2Hg + Br_2GeH_2 \xrightarrow[\text{(ref. 107)}]{} (CF_3Y)_2GeH_2$$

(Y = S, Se)

$$(CF_3Se)_2Hg + EBr_3 \xrightarrow[\text{(ref. 108)}]{} (CF_3Se)_3E$$

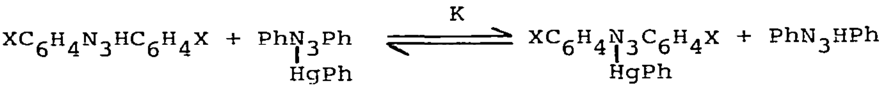
(E = P, As)

$$(CF_3Se)_2Hg + P_2I_4 \xrightarrow[\text{(ref. 108)}]{} P_2(SeCF_3)_4$$

$$(CF_3Se)_2Hg + PhPI_2 \xrightarrow[\text{(ref. 108)}]{} PhP(SeCF_3)_2$$

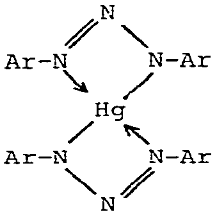
C. Mercurials with Nitrogen Substituents

Redistribution reactions between diphenylmercury and diverse mercury-nitrogen compounds and the reaction of PhHgOH with the corresponding N-H compound have served in the synthesis of diverse $PhHgN\langle$ products (109). Phenylmercury derivatives of amides (acetamide, propionamide, benzamide, N-2-pyridylacetamide, p-toluenesulfonamide, N-phenylmethanesulfonamide), imides, heterocycles (1*H*-benzotriazole, 2(1*H*)-pyridinone) and 1,3-diaryltriazenes were prepared. Other groups have reported investigations of mercury derivatives of 1,3-diaryltriazenes. Nesmeyanov studied exchange reactions involving 1,3-diaryltriazenes and their phenylmercury derivatives by proton NMR in chlorobenzene solution (110):



$$XC_6H_4N_3HC_6H_4X + \underset{HgPh}{PhN_3Ph} \xrightleftharpoons{K} \underset{HgPh}{XC_6H_4N_3C_6H_4X} + PhN_3HPh$$

Maire and his coworkers at Marseille have measured core binding energies (Cls, Nls, $Hg4f_{7/2}$, $Hg4f_{5/2}$) in seven mercurated triazenes of type 50 by X-ray photoelectron spectroscopy (111). The

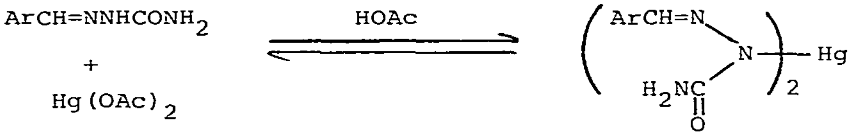


50

(Ar = C_6H_5 and p-XC_6H_4, where X = Me, MeO, Cl, Br, CN, $CH_3C(O)$, EtO_2C)

nitrogen atoms are all equivalent in 50 and the ionic character of the Hg-N bonds was used to explain the lack of effect of the *para* substituents on the C, N and Hg signals.

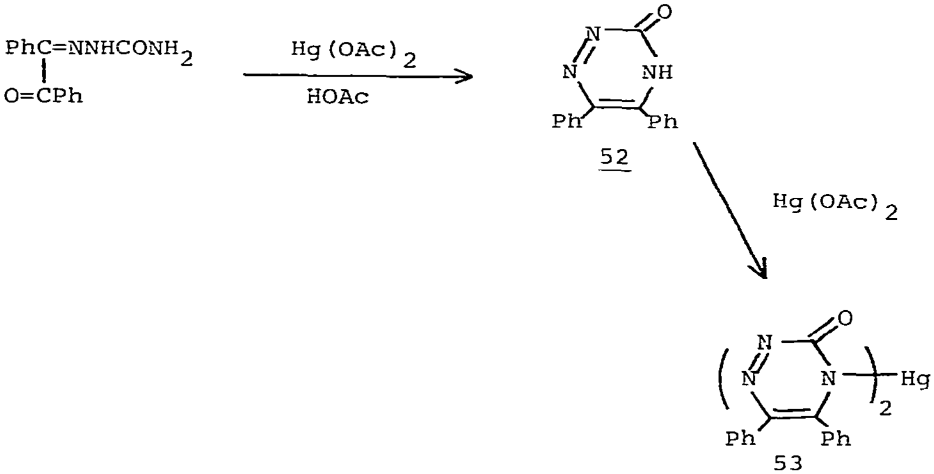
N-Mercurated products have been obtained by the action of mercuric acetate on semicarbazones (112):



51

Although the equilibrium above is unfavorable in acetic acid medium, addition of water, in which 51 is not soluble, forces the reaction to the right.

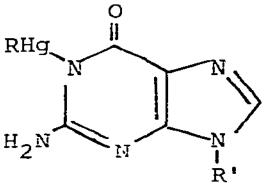
Separate experiments gave strong indication that 52 is an intermediate in the formation of 53.



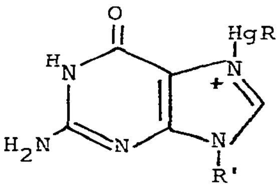
52

53

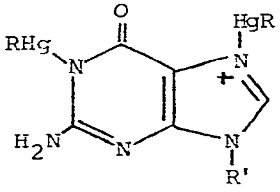
N-Methylmercuri and N-phenylmercuri derivatives of guanosine and thymidine have been prepared and studied using IR (for the solid complexes) and proton NMR (for their DMSO-d_6 solutions) spectroscopy to establish the sites of mercuration (113). The results are shown below.



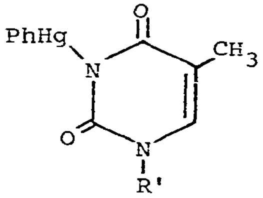
RHg($GuoH_{-1}$)



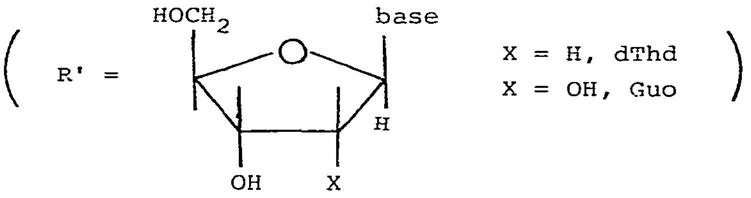
[RHgGuo]NO_3



[$(RHg)_2$Guo]NO_3



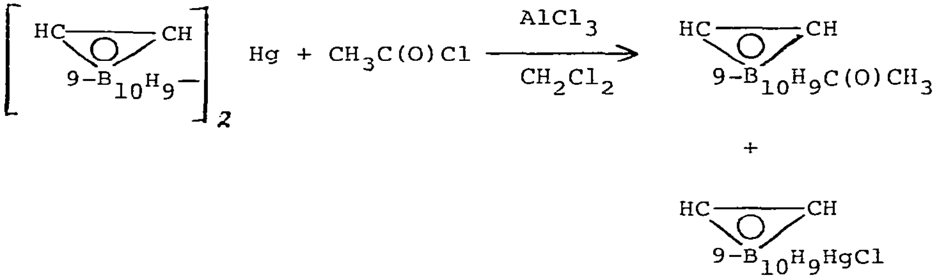
PhHg($dThdH_{-1}$)·H_2O



Proton NMR spectroscopy has been used to study the kinetics and equilibria of CH_3Hg-adenine interactions (114).

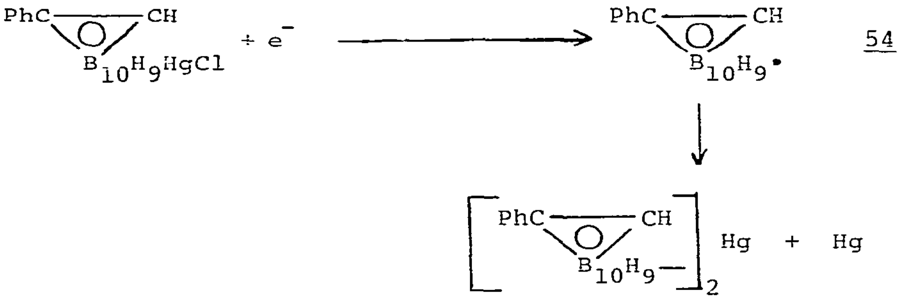
D. B-Mercurated Carboranes

B-Mercurated carboranes can be readily converted to B-acetyl carboranes (115):

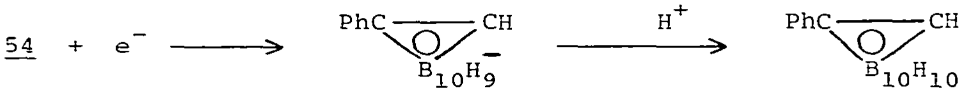


The electrochemical reduction of B-mercurated carboranes was studied by polarographic methods and suggested to proceed as follows (116);

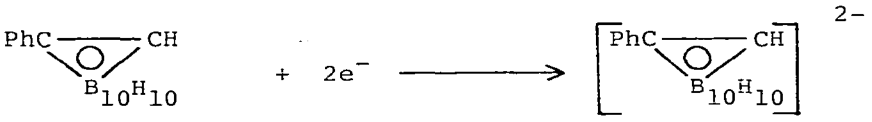
First wave:



Second wave:

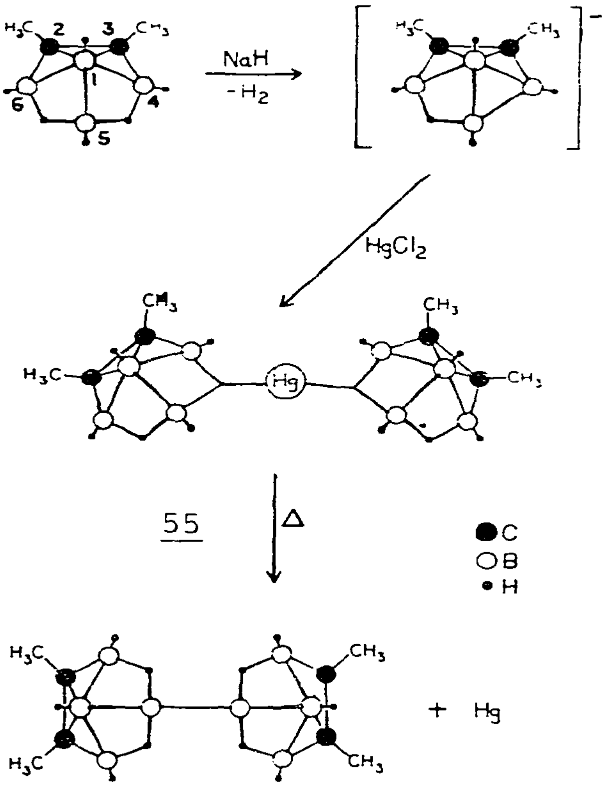


Third wave:



The potential required for the reduction of the B-Hg bond is much higher than that required for reduction of the C-Hg bond in C-mercurated carboranes.

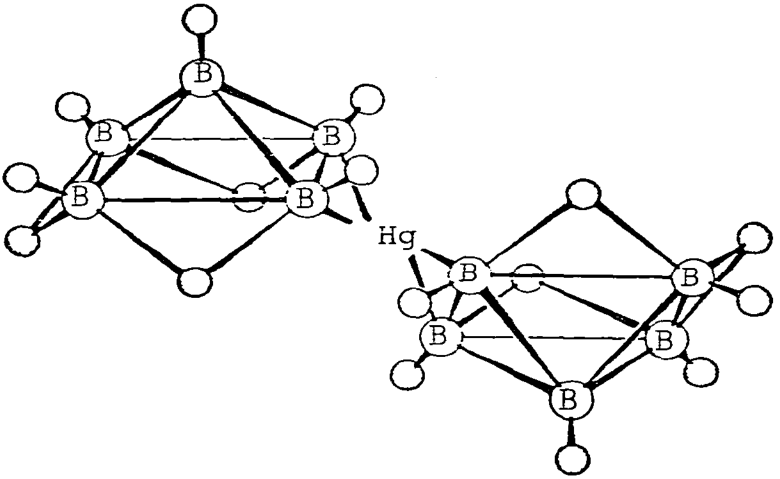
Hosmane and Grimes (117) have prepared $\mu,\mu'-(Me_2C_2B_4H_9)_2Hg$ as shown below:



55

56

Only the isomer of the product which has C_s symmetry is shown, although the product presumably is a mixture of the C_s and C_2 isomers. On thermolysis at 180°C, 55 extruded mercury and gave the bis-carborane, 56, as shown. Reaction of NaB_5H_8 with mercuric chloride in THF at -30°C gave the white, crystalline, sublimable mercurial $\mu,\mu'-(B_5H_8)_2Hg$, 57 (117). The structure shown is based on its proton and ^{11}B NMR spectra. This is the first mercury derivative of a pentaborane. Its thermolysis at 70°C for 20 hr. gave B_5H_9, a small amount of $(B_5H_8)_2$, elemental mercury and nonvolatile solids.



57

E. Mercurials with Group IV Substituents

The applications of silylmercurials, $(R_3Si)_2Hg$, as reagents in organic synthesis have been the subject of a review by Neumann and Reuter (118).

An improved synthesis of bis(trimethylsilyl)mercury has been reported (119). This simple preparation utilizes the reaction of trimethylchlorosilane, mercury and coarse aluminum sand in THF, with vigorous stirring for 5 hr., followed by sublimation (at 10^{-5} mm Hg, maximum temperature, 60°C). The reported yields range between 20 and 45%.

Bis(trifluorosilyl)mercury has been prepared by cocondensation of trifluorosilyl radicals (from Si_2F_6 *via* radio-frequency glow discharge) and mercury vapor in 26% yield (14). The product was described as a white solid, which, curiously, was insoluble in all organic or inorganic solvents tried.

Also prepared by the more conventional hydride route have been $[(Cl_3Si)_3Si]_2Hg$ and $\{[(MeO)_3Si]_3Si\}_2Hg$ (120):

$$2\ (X_3Si)_3SiH + (Me_3C)_2Hg \xrightarrow{70°C} [(X_3Si)_3Si]_2Hg + 2\ Me_3CH$$

(X = Cl, 48% yield)
(X = OMe, 80% yield)

Both mercurials are white, sublimable solids. Photolysis resulted in extrusion of mercury:

$$[(X_3Si)_3Si]_2Hg \xrightarrow[\text{hexane}]{h\nu} (X_3Si)_3Si\text{-}Si(SiX_3)_3 + Hg$$

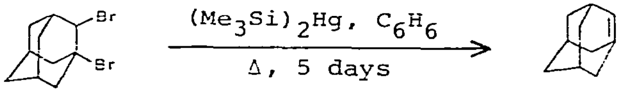
The hydride procedure also served in the preparation of $[(C_6F_5)_3Sn]_2Hg$ (121):

$$2\ (C_6F_5)_3SnH + Et_2Hg \xrightarrow[\text{(exothermic)}]{\text{hexane}} [(C_6F_5)_3Sn]_2Hg + 2\ C_2H_6$$

In contrast to most $(R_3Sn)_2Hg$ compounds, $[(C_6F_5)_3Sn]_2Hg$ is quite stable and melts without decomposition at 171-173°C. Its reaction with $[(Me_3SiCH_2)_3Sn]_2Hg$ in toluene at room temperature proceeded with loss of elemental mercury, giving the unsymmetrical distannane, $(C_6F_5)_3SnSn(CH_2SiMe_3)_2$. The reaction products of $[(C_6F_5)_3Ge]_2Hg$ and $[(C_6F_5)_3Sn]_2Hg$ with $(Ph_3P)_3Pt$, i.e., complexes of type $(C_6F_5)_3MHgPt(PPh_3)_2M(C_6F_5)_3$ (M = Ge, Sn), could be analyzed and separated very well using liquid-solid chromatography (122).

Although $(C_6F_5)_3SnHgCl$ is unstable (121), a stable 1:1 2,2'-bipyridine adduct could be prepared by the electrochemical oxidation of mercury in a CH_3CN/C_6H_6 solution of triphenyltin chloride and 2,2'-bipyridine (123). The far IR spectrum of this product was measured and bands at 272 and 155 cm^{-1} were assigned to ν(Hg-Cl) and ν(Hg-Sn), respectively.

Group IV-substituted mercurials are finding useful synthetic application as their chemistry is being developed. They may be used to effect intra- and intermolecular dehalogenation in organic and inorganic systems:



58

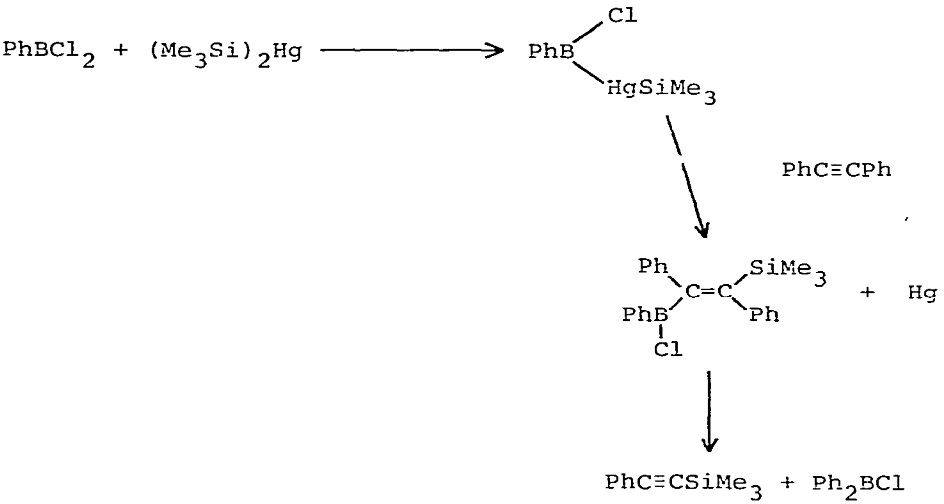
Adamantene, 58, an anti-Bredt olefin, was thus generated in the presence of suitable trapping agents, e.g., diphenylisobenzofuran and 2,5-dimethylfuran (124).

$$X_2PCl \xrightarrow[C_6H_6,\ rt]{(Me_3Si)_2Hg} X_2P{-}PX_2 + 2\ Me_3SiCl + Hg \quad (X = RO,\ Et_2N,\ Ph)$$

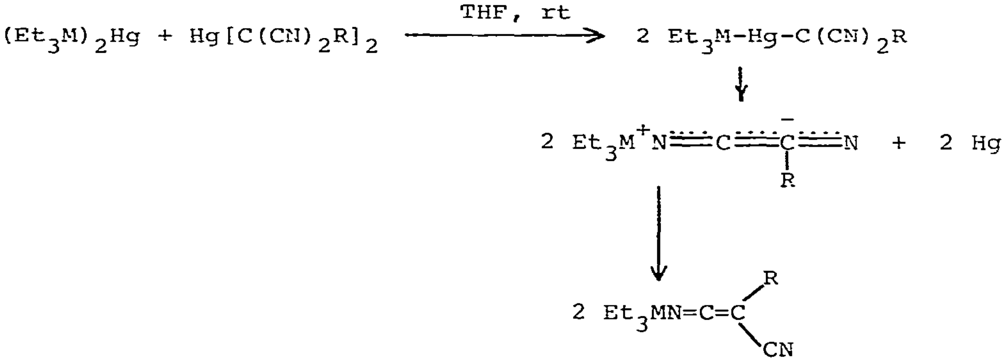
(ref. 125)

$$RBX_2 \xrightarrow{(Me_3Si)_2Hg} Hg + 2\ Me_3SiX + \text{"RB"}$$

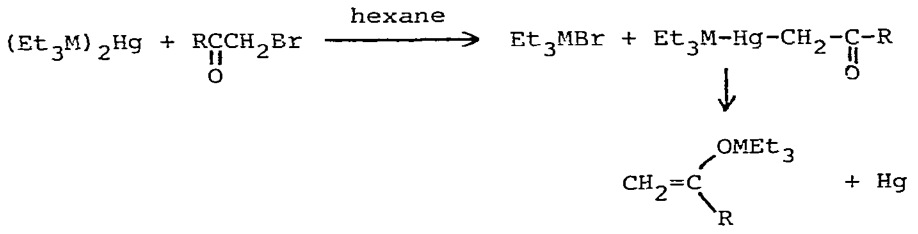
The "RB" intermediate underwent polymerization or insertion into C-H bonds (126). Attempts to trap "RB" with diphenylacetylene apparently resulted in the trapping of an earlier mercury-containing intermediate. At any rate, the final, mercury-free products could be rationalized in this way:



Other organic syntheses have been described.
Synthesis of N-metalated ketene imines (127);

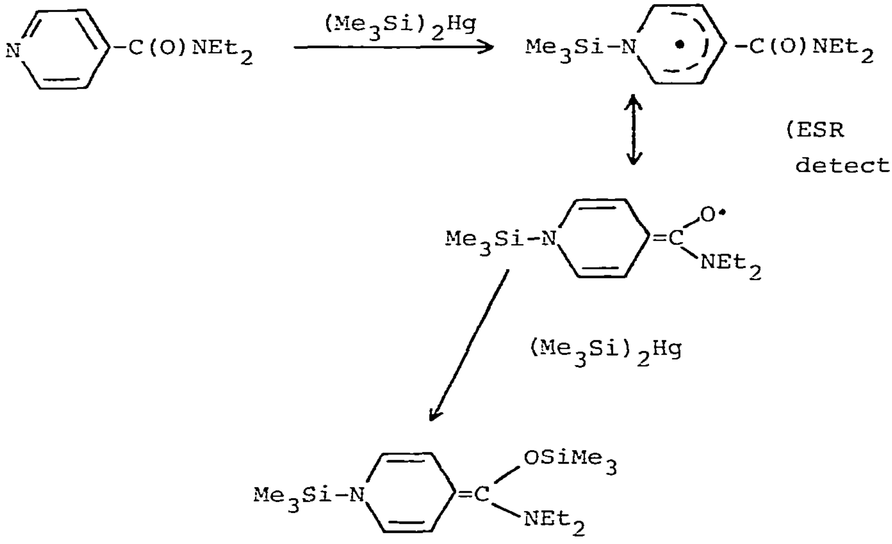


Synthesis of O-metalated enols (128):

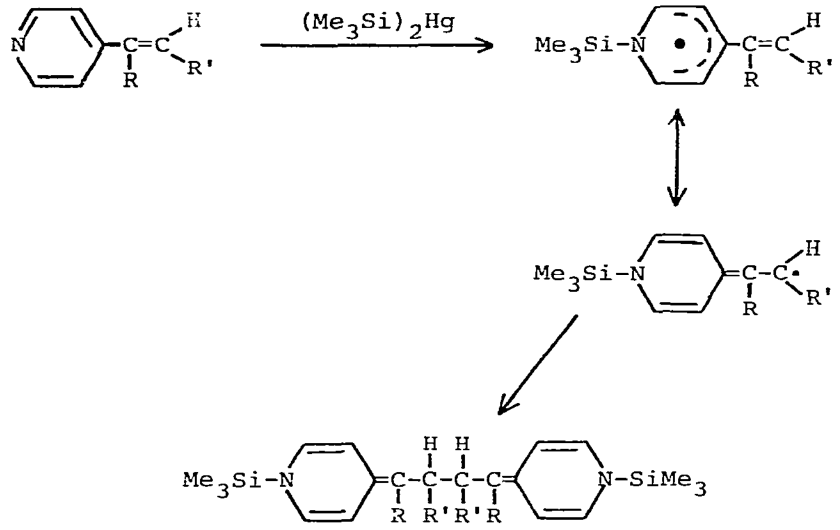


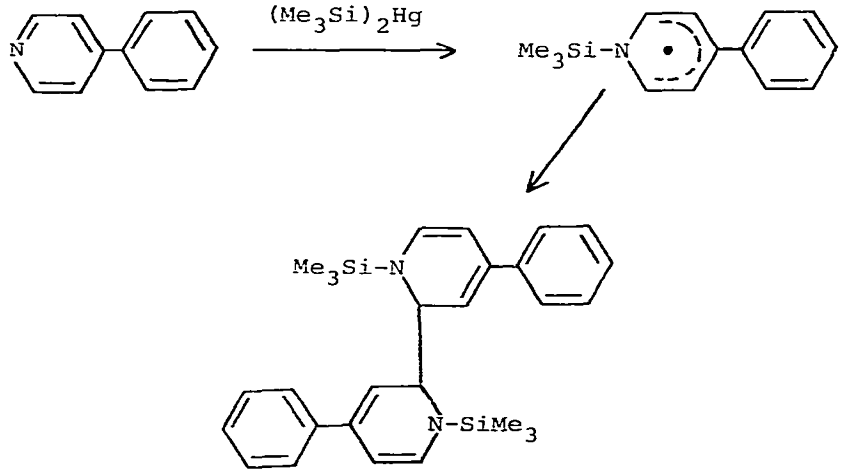
When R = C_6F_5, a rapid reaction occurred below room temperature, but for R = C_6H_5 a 15 min. reaction time at 85°C was required.

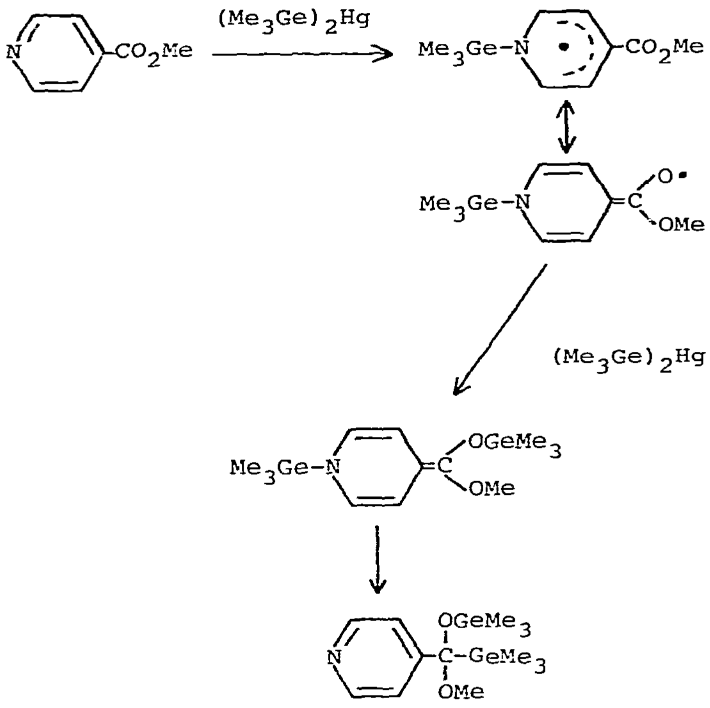
In the generation of pyridinyl radicals (129):



(ESR detectable)

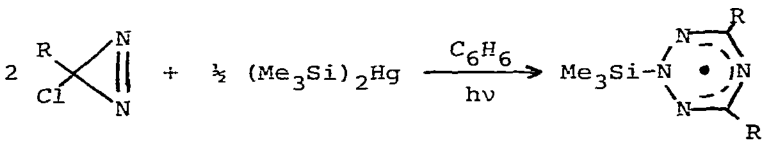

(Me$_3$Si)$_2$Hg


(Me$_3$Si)$_2$Hg



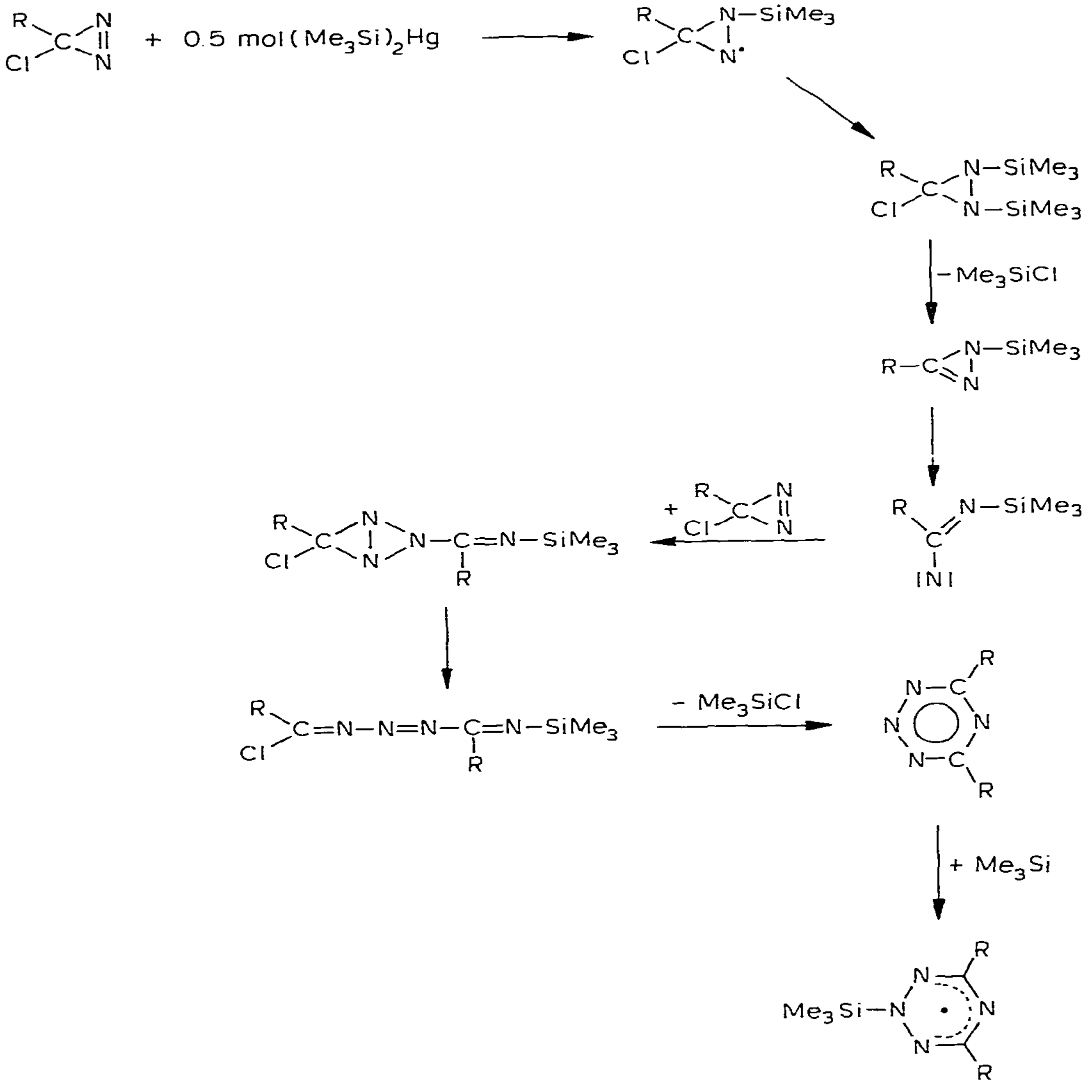
Many of these reactions proceed exothermally at room temperature, others require heating. The reactions also can be induced by UV irradiation. The mechanism of the latter process was shown not to involve free trimethylsilyl radicals, rather a long-lived photoexcited polar state of $(Me_3Si)_2Hg$ which is complexed stepwise by two molecules of pyridine (130). Only in the last step are free radicals formed.

In the generation of radicals from 3-chlorodiazirines (131).



59

The following reaction course was proposed for the formation of 59:



F. Organomercurials with Transition Metal Substituents

Organomercury derivatives of iron, cobalt and tungsten have been prepared by Glockling et al. (132):

$$2\ RHgCl + Fe(CO)_4{}^{2-} \longrightarrow \underline{cis}\text{-}(RHg)_2Fe(CO)_4 + 2\ Cl^-$$

$(R = Me_3SiCH_2,\ (Me_3Si)_2CH,\ (Me_3Si)_3C\ )$

$$Me_3SiCH_2HgCl + Co(CO)_4{}^- \longrightarrow Me_3SiCH_2HgCo(CO)_4$$

$$Me_3SiCH_2HgCl + CpW(CO)_3{}^- \longrightarrow Me_3SiCH_2HgW(CO)_3Cp$$

The iron complexes underwent symmetrization with varying facility:

$$n\ (RHg)_2Fe(CO)_4 \longrightarrow n\ R_2Hg + [HgFe(CO)_4]_n$$

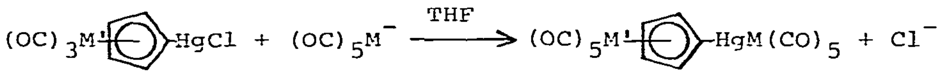
($R = Me_3SiCH_2$, slow in $CDCl_3$ at room temperature; $R = (Me_3Si)_2CH$, rapid; $R= (Me_3Si)_3C$, not at all; stable to 150°C).

$[(Me_3Si)_3CHg]_2Fe(CO)_4$ was cleaved by mercuric bromide at room temperature:

$$[(Me_3Si)_3CHg]_2Fe(CO)_4 + HgBr_2 \longrightarrow (Me_3Si)_3CHgBr + [HgFe(CO)_4]_n$$

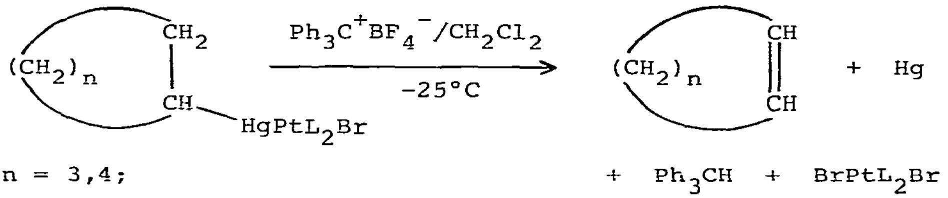
The cobalt-mercury complex underwent slow symmetrization at room temperature (rapid at 80°C), giving $Hg(CH_2SiMe_3)_2$ and $Hg[Co(CO)_4]_2$. The symmetrization of the tungsten complex was fast enough at room temperature to prevent its isolation in good purity.

Russian workers have prepared organomercurials containing Mn-Hg and Re-Hg bonds (133):



(M, M' = Mn, Re)

Compounds containing a Pt-Hg bond were found to react readily with $Ph_3C^+BF_4{}^-$ (134):

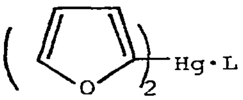


(n = 3,4;
L = Ph₃P)

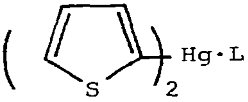
A β hydride abstraction is involved in this reaction.

8. COMPLEXES OF ORGANOMERCURIALS.

The first Lewis base complexes of heterocyclic organomercurials have been reported (135):



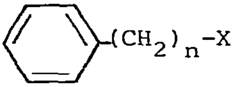
L = 1,10-phenanthroline,
3,4,7,8-Me_4-1,10-phenanthroline
2,9-Me_2-1,10-phenanthroline



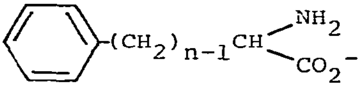
L = 2,9-Me_2-1,10-phenanthroline

Both mercurials are relatively weak Lewis acids, with difurylmercury being the stronger of the two. IR, ^1H NMR and mass spectra of the complexes were studied. They also were subjected to DTA and TG examination. Neither mercurial formed isolable complexes with 2,2'-bipyridyl, $Ph_2PCH_2CH_2PPh_2$, Ph_3P or $MeSCH_2CH_2SMe$.

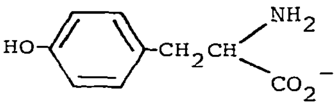
A CH_3Hg(II)-arene interaction was observed (NMR studies) in mercurials of type CH_3HgL, with L=



(X = NH_2, S^-; n = 1,2)



(n = 2,3)



For these CH_3HgL complexes a high field shift of the CH_3Hg resonance was observed and this was rationalized in terms of an anisotropic shielding effect due to an intramolecular interaction between Hg and the phenyl ring (136). This type of interaction had been found in the solid state structure of N-bonded methyl(L-tyrosinato)mercury (II) (cf. 1978 Annual Survey, J. Organometal. Chem., 183 (1979) 239).

Canadian workers (137) have prepared and studied complexes of mercuric cyanide with tertiary phosphines:

$(R_3P)_nHg(CN)_2$ R = Ph, n = 1, 2
p-$CH_3C_6H_4$, n = 1, 2
cyclo-C_6H_{11}, n = 1,2
t-C_4H_9, n = 1

Tri-o-tolylphosphine did not form a stable complex with $Hg(CN)_2$, presumably for steric reasons. Solution molecular weight and conductance studies and vibrational and NMR (^1H, ^{31}P) spectroscopic measurements were carried out. Evidence was obtained in favor of a dimeric structure for $(cyclo\text{-}C_6H_{11})_3P\cdot Hg(CN)_2$, with bridging and terminal CN groups.

Also prepared and studied in much the same way were 1:1 and 2:1 tertiary phosphine complexes of mercuric acetate (phosphine = $(p\text{-}CH_3C_6H_4)_3P$, $(p\text{-}FC_6H_4)_3P$, Ph_2MeP, Ph_2Et_2P) and the 1:1 $(o\text{-}CH_3\text{-}C_6H_4)_3P\text{-}Hg(OAc)_2$ adduct (138), as well as 1:1 and 2:1 complexes of triphenylphosphine with $(CH_3CO_2)_2Hg$, $(CH_2FCO_2)_2Hg$, $(CHF_2CO_2)_2$- and $(CF_3CO_2)_2Hg$ (139). Reported also have been two detailed ^{31}P NMR studies of tertiary phosphine complexes of Hg(II) compounds (140).

Of interest also is the reaction of dimethylchlorophosphine with elemental mercury (141):

$$Me_2PCl + Hg \xrightarrow{80°,\ \text{several days}} (Me_2P\text{-}PMe_2\cdot HgCl_2)_x$$

The product is a coordination polymer, is insoluble in all usual solvents and is chemically quite stable. Thermolysis gave mer-

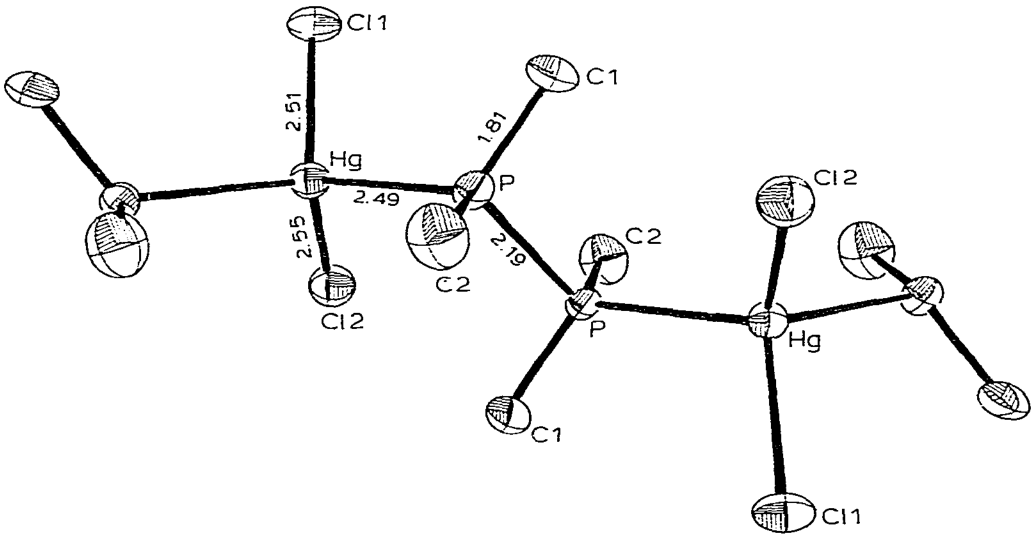
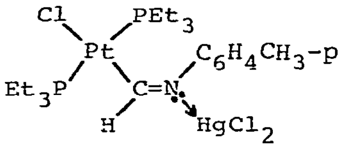


Figure 1. ORTEP Plot of two molecular units of $(Me_2P\text{-}PMe_2\cdot HgCl_2)_x$
(From F. Seel and H. W. Heyer, Z. anorg. allg. Chem., 456 (1979) 217).

cury and very pure Me_2PCl; hydrolysis gave Me_2PH and Me_2PHO. An X-ray diffraction study was carried out. Figure 1 shows two repeating units of the structure.

Finally, mention is made of mercuric halide complexes of triphenylphosphineimine, $Ph_3P{=}NH{\cdot}HgX_2$ (142) and of the novel adduct 60 (143).



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9. STRUCTURAL STUDIES OF ORGANOMERCURIALS AND RELATED COMPOUNDS.

The structures of some bona fide organomercury compounds as well as of some mercurials without a C-Hg bond, which, however, may be of interest to the readers of this Survey, have been determined by means of X-ray diffraction.

Dibenzylmercury, $(PhCH_2)_2Hg$ (144) (Figure 2). As expected, <C-Hg-C is essentially linear, 177.7(16)° and d(C-Hg) = 2.065(17)Å.

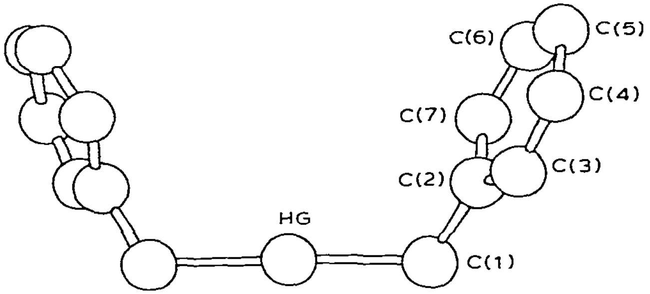

Figure 2. The molecular structure of dibenzylmercury. From P. B. Hitchcock, Acta Cryst. B 35 (1979) 746.

Di(2-thienyl)mercury, 61 (145) (Figure 3). In this molecule the C-Hg-C angle is exactly 180° and d(C-Hg) = 2.061(18)Å. There are no Hg....S interactions in the crystal, d(Hg....S) = 3.619(5)Å.

The 1:1 adduct of $(ClCH_2C{\equiv}C)_2Hg$ and 1,10-phenanthroline (146) Figure 4). Two crystallographically independent molecules are contained in the asymmetric unit; the C-Hg-C angle is 165° in one, 168° in the other, a significant deviation from linearity resulting from adduct formation. The mercury coordination has distorted tetrahedral symmetry. There are no Hg....Cl interactions.

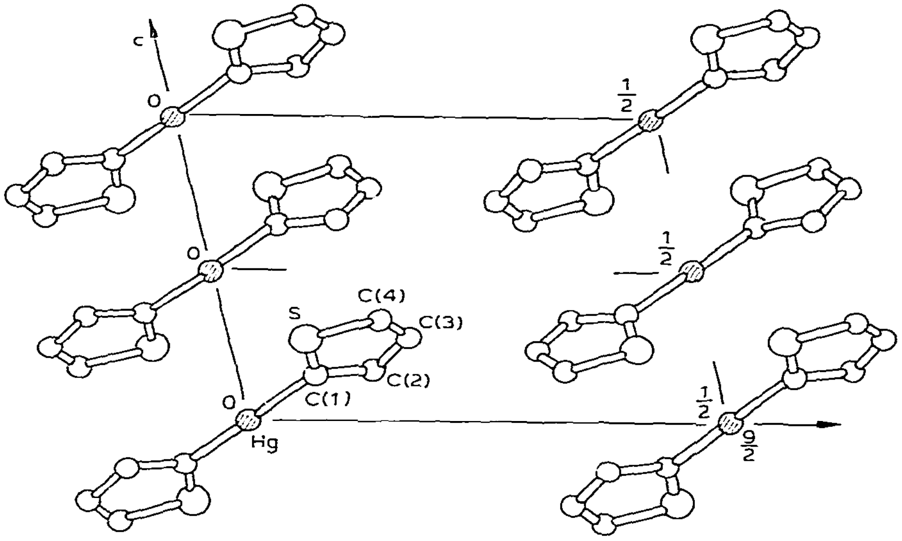

Figure 3. The molecules of di(2-thienyl)mercury in the crystal structure viewed along the b axis. From D. Grdenić, B. Kamenar and V. Žeželj, Acta Cryst. B 35 (1979) 1889.

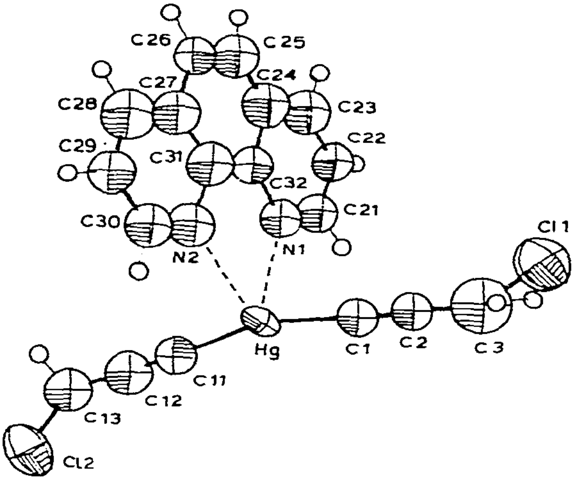

Figure 4. ORTEP drawing of the 1:1 adduct of $(ClCH_2C{\equiv}C)_2Hg$ and 1,10-phenanthroline. From E. Gutiérrez-Puebla, A. Vegas and S. García-Blanco, Cryst. Struct. Comm. 8 (1979) 861.

Chloromercuriacetaldehyde, $ClHgCH_2CH{=}O$ (147) (Figure 5). In this molecule the C-Hg-C angle is 172.2(5)°, d(C-Hg) = 2.11(2)Å and d(Cl-Hg) = 2.326(6)Å. There is no intramolecular Hg....O interaction, but there are two intermolecular Hg....O contacts of 2.84(2) and 2.87(1)A. There is a possible intermolecular Hg....Cl contact (3.370(6)Å.

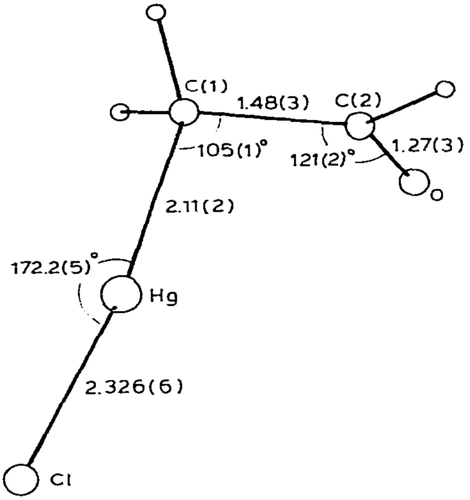

Figure 5. The molecular structure of chloromercuriacetaldehyde. From J. Halfpenny and R. W. H. Small, Acta Cryst. B 35 (1979) 1239.

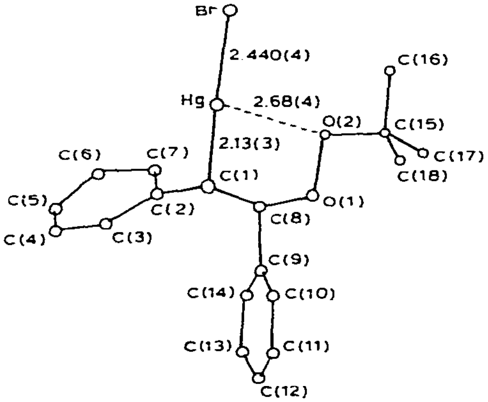

Figure 6. The molecular structure of threo-1-bromomercuri-2-t-butylperoxy-1,2-diphenylethane. From J. Halfpenny and R. W. H. Small, J. Chem. Soc., Chem. Comm. (1979) 879.

threo-1-Bromomercuri-2-t-butylperoxy-1,2-diphenylethane, the t-butylperoxymercuration product of cis-stilbene, $PhCH(OOCMe_3)CHPh(HgBr)$ (148) (Figure 6). There is an intramolecular Hg....O contact in this molecule of 2.68(4)Å. The configuration about the central C-C bond is shown in Figure 7. The C-Hg-Br angle is 177(1)°.

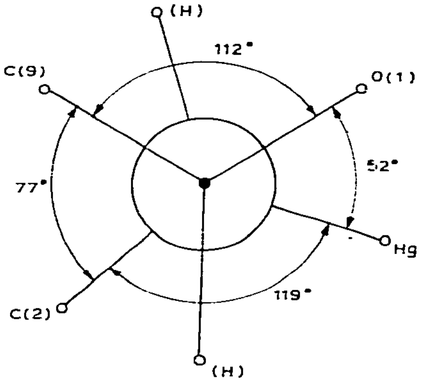

Figure 7. Configuration about the central C-C bond of threo-1-bromomercuri-2-t-butylperoxy-1,2-diphenylethane showing torsional angles. From J. Halfpenny and R. W. H. Small, J. Chem. Soc., Chem. Comm. (1979) 879.

The 2:1 Methylmercury complexes with adenine and 9-methyladenine (149) (Figures 8 and 9). This paper brings the first crystallographic evidence for metal-adenine interactions involving the amino group.

(Creatinine)phenylmercury(II) nitrate monohydrate (150) (Figure 10). The C-Hg-N bond is nonlinear (174(1)°) and there is a weak Hg....O interaction between the mercury atom and a nitrate anion.

Bis[2,3,4,5-tetrakis(trifluoromethylthio)pyrrolyl]mercury, $Hg[NC_4(SCF_3)_4]_2$ (151) (Figure 11). The N-Hg-N bond angle is 180°. The pyrrolyl rings and the Hg atom are coplanar within 0.02Å. There are no intermolecular Hg....F or Hg....S interactions.

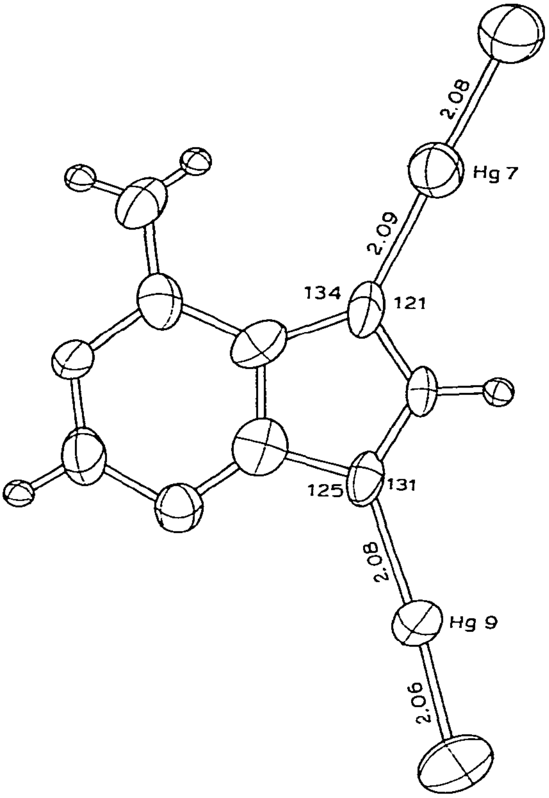

Figure 8. The structure of the $[(CH_3Hg)_2(\text{adenine})]^+$ ion in the nitrate salt. From L. Prizant, M. J. Olivier, R. Rivest and A. L. Beauchamp, J. Amer. Chem. Soc., 101 (1979) 2756.

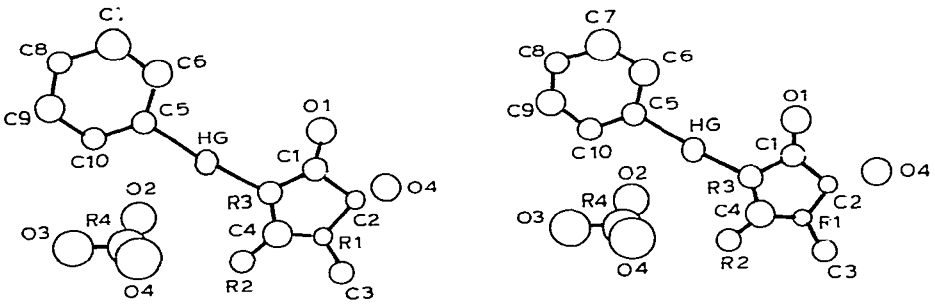

Figure 10. Structure of (creatinine)phenylmercury(II) nitrate monohydrate. From A. J. Canty, N. Chaichit and B. M. Gatehouse, Acta Cryst. B 35 (1979) 592.

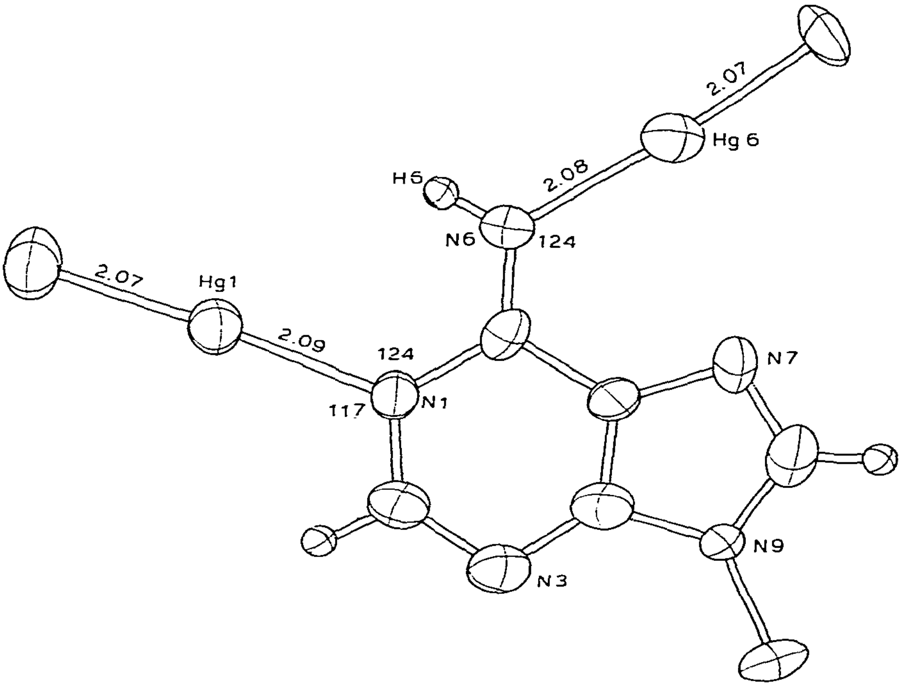

Figure 9. The structure of the [(CH$_3$Hg)$_2$(9-methyladenine)]$^+$ ion in the perchlorate salt. From L. Prizant, M. J. Olivier, R. Rivest and A. L. Beauchamp, J. Amer. Chem. Soc., 101 (1979) 2765.

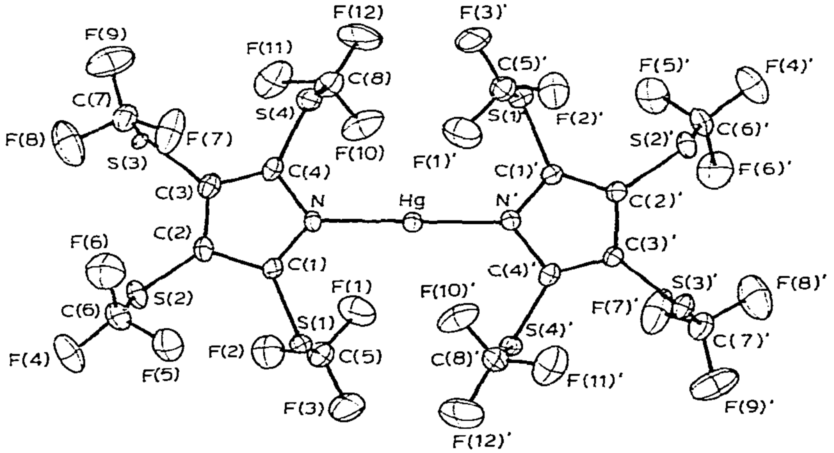

Figure 11. Molecular structure of bis(2,3,4,5-tetrakis(trifluoromethylthio)pyrrolyl)mercury showing 20% probability ellipsoids. Form D. J. Brauer, Acta Cryst. B 35 (1979) 1770.

Phenylmercury(II) dithizonate (yellow form) (152) (Figure 12). In this study a series of organomercury dithizonates, RHg(HDz) (R = CH_3, Ph, 4-MeC_6H_4, 2,6-$Me_2C_6H_3$) was prepared. Like $Hg(HDz)_2$, all showed photochromism when irradiated in organic solution (yellow $\rightleftharpoons$ blue). Attempts to obtain a crystalline sample of the blue form were unsuccessful.

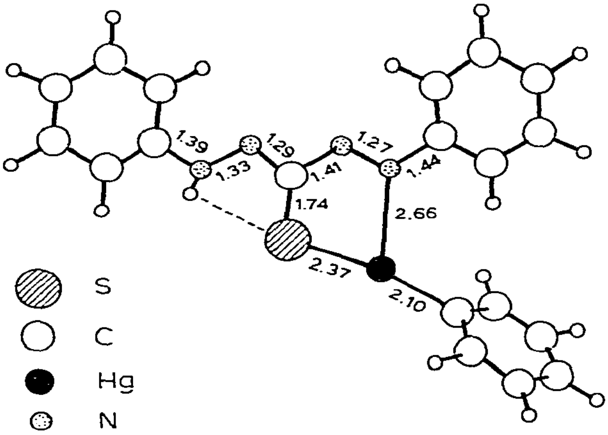

Figure 12. Molecular structure of phenylmercury(II) dithizonate. The dashed line indicates a hydrogen bond. The molecule is essentially planar except for the Hg-phenyl ring which is twisted out of this plane by about 60°. From A. T. Hutton and H. M. N. H. Irving, J. Chem. Soc., Chem. Comm. (1979) 1113.

Various RSHg(II) complexes: Polymeric $CH_3SHgOAc\cdot\gamma$-picoline (Figure 13) and $C_2H_5SHgOAc\cdot$pyridine (Figure 14); also$(t\text{-}BuS)_4Cl_4Hg_4$-(γ-picoline)$_2$(Figure 15) and CH_3SHgBr (Figure 16) (153). CH_3SHgCl is isomorphous with the bromide (154)

Mercury(II) N,N-diisopropyldithiocarbamate (α-form), $Hg(S_2CNPr^i{}_2)_2$ (155) (Figure 17). The molecules exist as monomers in the crystal and have chelating dithiocarbamato ligands.

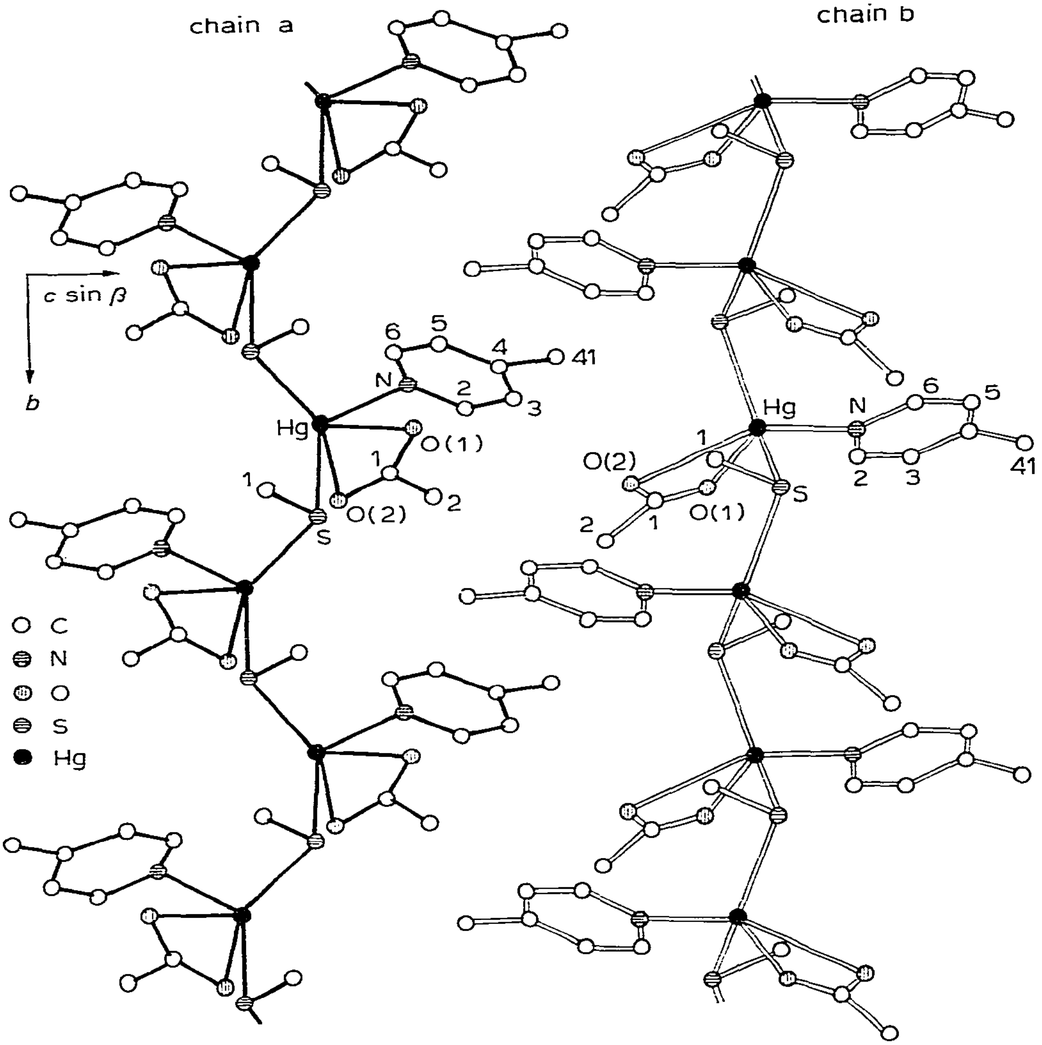

Figure 13. Projection of the structure of $CH_3SHgO_2CCH_3 \cdot \gamma$-picoline along a, showing the two independent polymeric strands. From A. J. Canty, C. L. Raston and A. H. White, Aust. J. Chem., 32 (1979) 311.

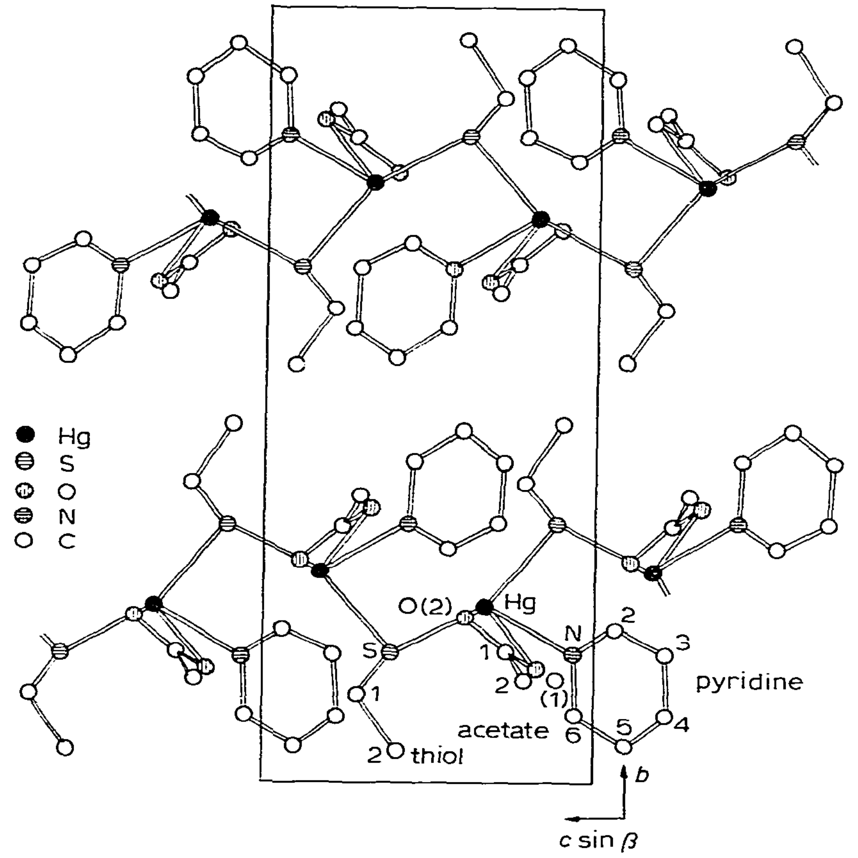

Figure 14. Projection of the structure of $C_2H_5SHgO_2CCH_3 \cdot C_5H_5N$ along *a*. From A. J. Canty, C. L. Raston and A. H. White, Aust. J. Chem., 32 (1979) 311.

1,5,9,13-Tetrathiacyclohexadecane-mercury(II) perchlorate (156) (Figure 18). In this complex the mercury atom is encircled by a novel macrocyclic ligand.

A selenourea complex of methylmercuric nitrate, $[CH_3HgSeC(NH_2)_2]$-NO_3 (157) (Figure 19). The mercury atom is approximately linearly coordinated to carbon and selenium, with strong Hg-Se bonding.

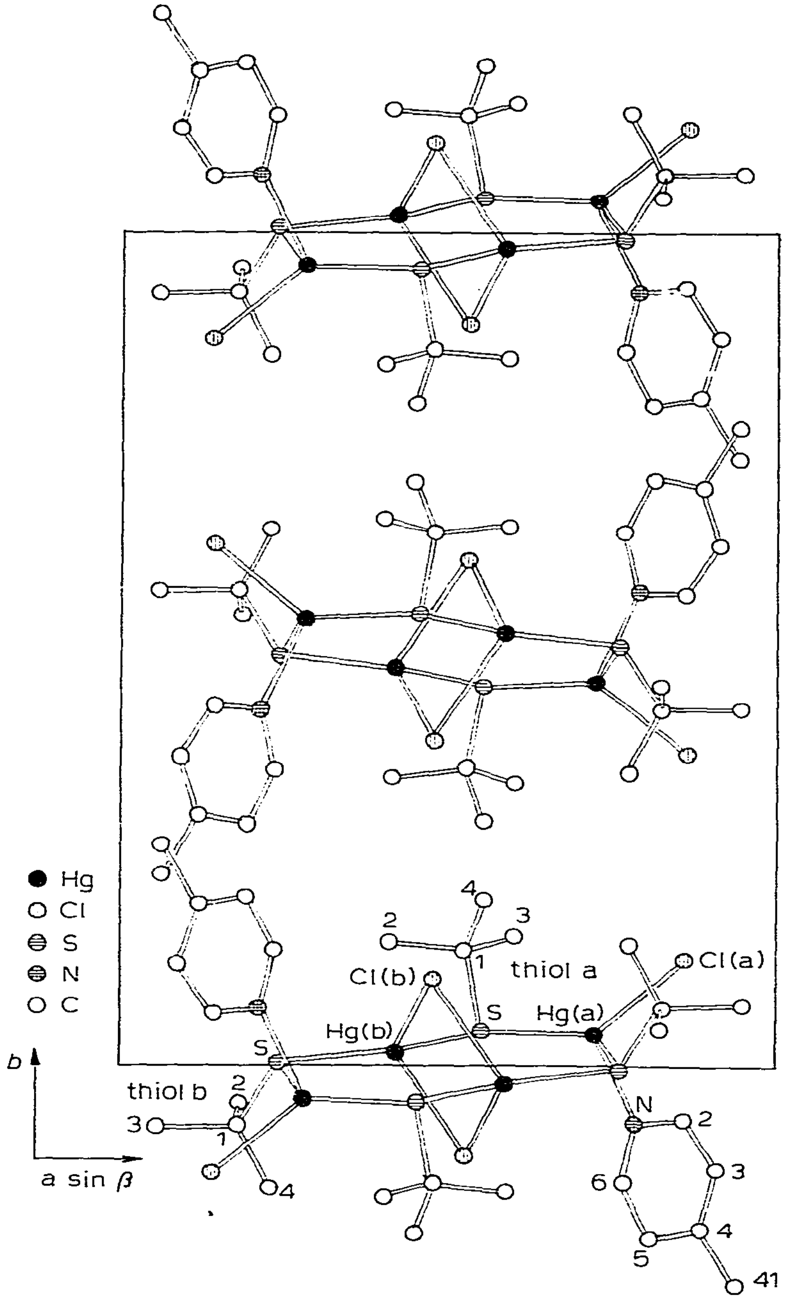

Figure 15. Projection of the structure of $(t\text{-BuS})_4Cl_4Hg_4(\gamma\text{-picoline})_4$ along c. From A. J. Canty, C.L. Raston and A. H. White, Aust. J. Chem., 32 (1979) 311.

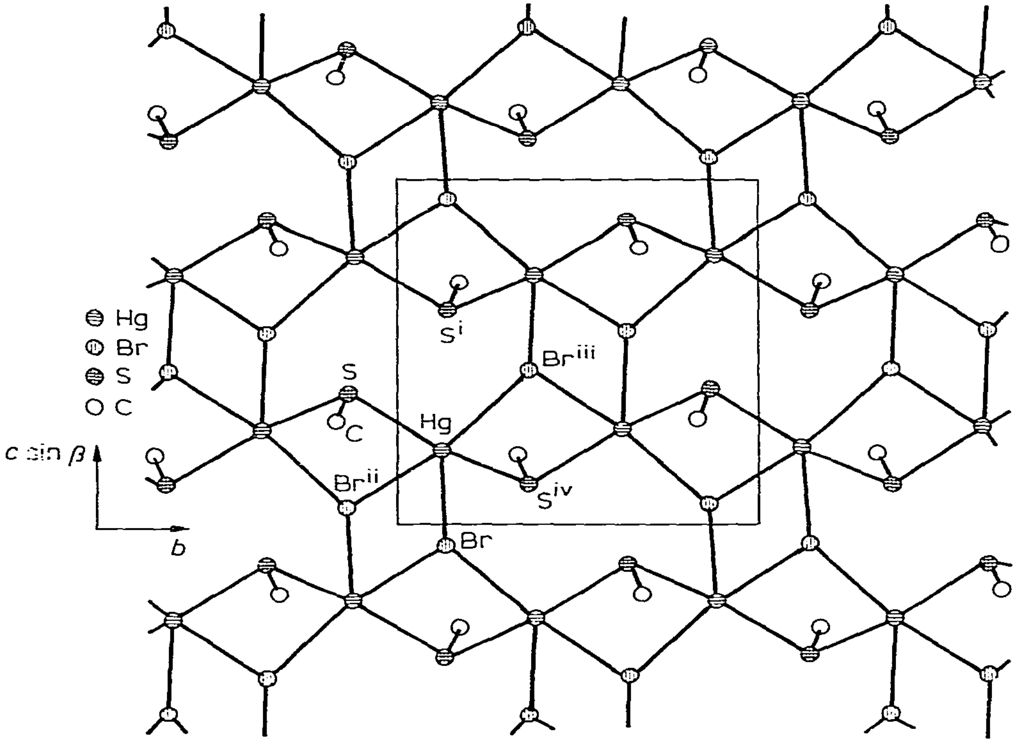

Figure 16. Projection of the structure of CH_3SHgBr along a. From A. J. Canty, C. L. Raston and A. H. White, Aust. J. Chem., 32 (1979) 311.

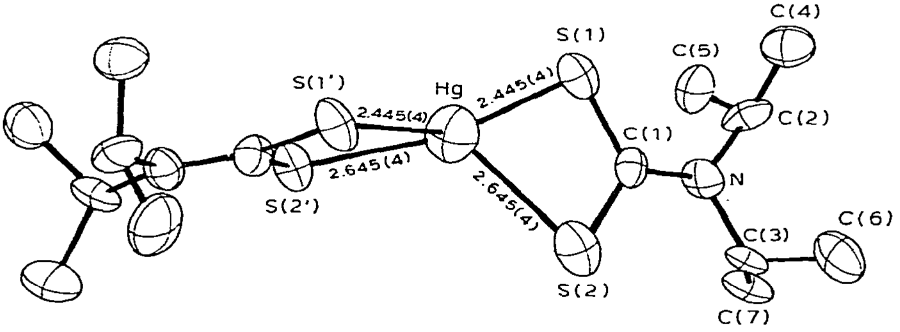

Figure 17. Molecular structure of mercury(II) N,N-diisopropyldithiocarbamate, α-form. The thermal ellipsoids are at the 50% probability level. From M. Ito and H. Iwasaki, Acta Cryst. B 35 (1979) 2720.

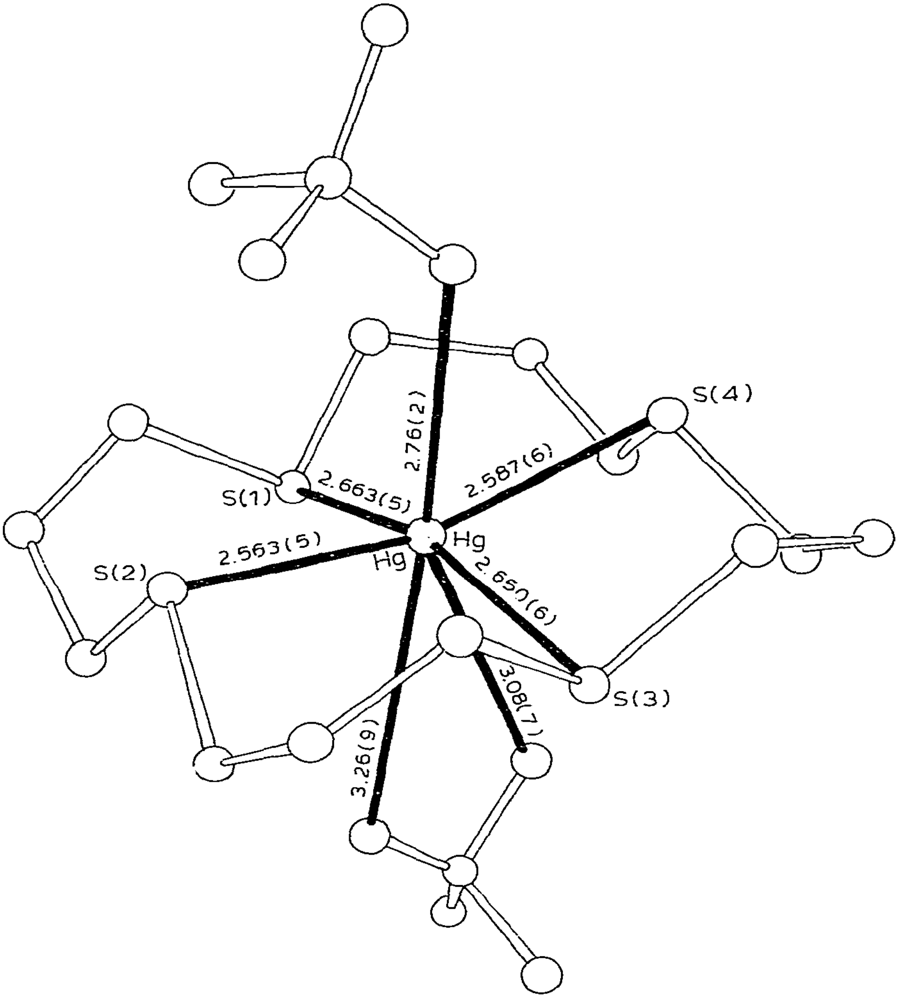

Figure 18. Molecular structure of 1,5,9,13-tetrathiacyclohexadecane-mercury(II) perchlorate. From T. E. Jones, L. S. W. L. Sokol, D. B. Rorabacher and M. D. Glick, J. Chem. Soc., Chem. Comm. (1979) 140.

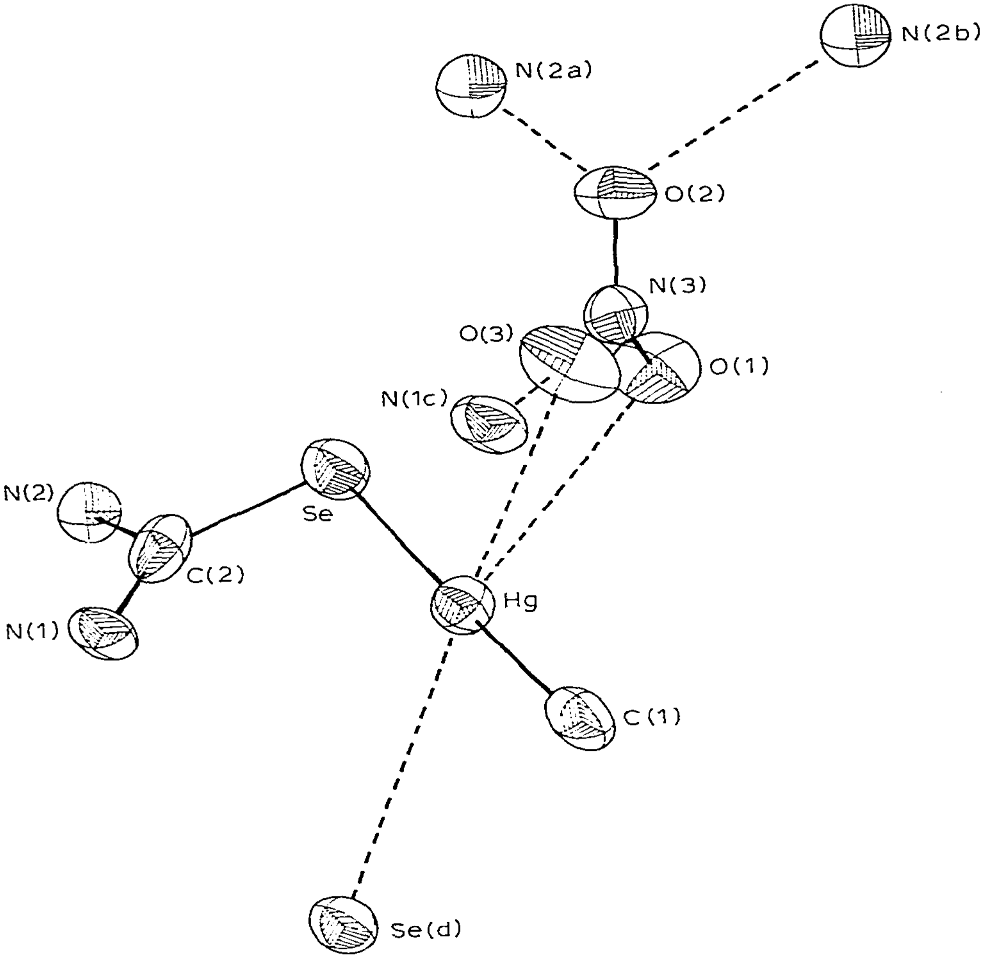

Figure 19. The molecular structure of $[CH_3HgSeC(NH_2)_2]NO_3$. Ellipsoids are drawn at the level of 50% probability. From A. J. Carty, S. F. Malone and N. J. Taylor, J. Organometal. Chem., 172 (1979) 201.

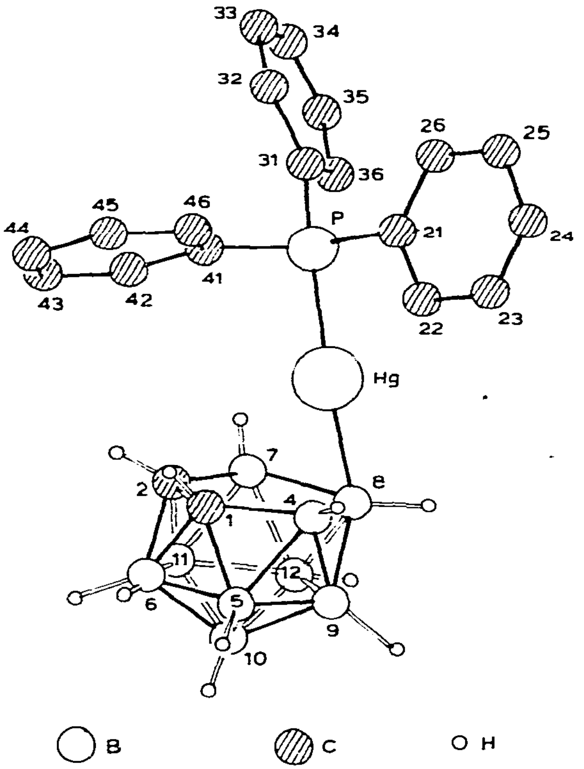

Figure 20. Molecular structure of 3-triphenylphosphine-3-mercura-1,2-dicarbadodecaborane(11). From H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, J. Chem. Soc., Dalton Trans. (1979) 619.

3-Triphenylphosphine-3-mercura-1,2-dicarbadodecaborane(11)·dioxane (158) (Figure 20). The mercury is bonded to a boron atom. This compound was prepared by reaction of $(Ph_3PHgCl_2)_2$ with $Tl[B_9C_2{}^{1,2}\text{-}Tl^{3}H_{11}]$ in THF and isolated in the form of a colorless solid. Also prepared were salts of the $[B_9C_2{}^{1,2}(HgMe)^{3}H_{11}]^-$ and the $[B_9\text{-}C_2{}^{1,2}(HgPh)^{3}H_{11}]^-$ anions, as well as $3,3'\text{-}Hg[B_9C_2{}^{1,2}(py)^{4}H_{10}]_2$, for which the structure shown in Figure 21 was proposed.

The trimesitylphosphine-mercury(II) nitrate dimer (159)(Figure 22)

The asymmetric unit contains two independent half-dimers.

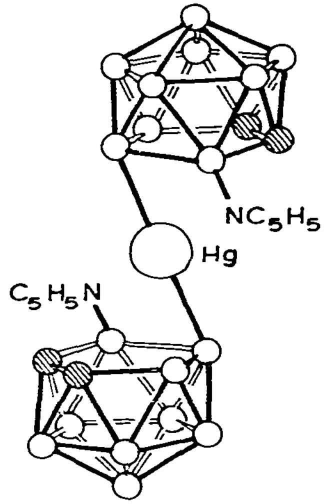

Figure 21. Proposed structure of $Hg[B_9C_2pyH_{10}]_2$. From H. M. Colquhoun, T. J. Greenhough and M. G. H. Wallbridge, J. Chem. Soc., Dalton Trans. (1979) 619.

10. SPECTROSCOPIC STUDIES OF ORGANOMERCURY COMPOUNDS.

A. Vibrational Spectroscopy

The IR and Raman spectra of CF_3HgCH_3 and CF_3HgCD_3 have been studied in the gas and in the liquid phase (160). A normal coordinate analysis gave the stretching force constants f(Hg-CF_3) = 2.04 N cm^{-1} and f(Hg-CH_3) = 2.52 N cm^{-1}; i.e., the effect of the CF_3 substituent (compared to CH_3) is to strengthen the Hg-CH_3 bond. Gas → liquid phase shifts of the CF_3 stretching modes indicated significant intermolecular Hg....F interactions. Vibrational spectra of $CH_3HgC{\equiv}CCH_3$, $CD_3HgC{\equiv}CCH_3$, $CH_3HgC{\equiv}CCD_3$ and $CD_3HgC{\equiv}CCD_3$ also were recorded in solution (CCl_4, CS_2, C_6H_6) and in the solid state at -196°C (161). A stretching force constant of f(Hg-CH_3) = 2.48 N cm^{-1} was obtained . Thus the $CH_3C{\equiv}C$ substituent also strengthens the Hg-CH_3 bond. Similar spectroscopic studies were carried out with CH_3HgCN and CD_3HgCN (IR in CCl_4, CS_2, $CHCl_3$ and C_6H_6 solution and on the solid state at -196°C; Raman in C_6H_6 and H_2O solution and on the melt)(162). Here a normal coordinate analysis gave f(Hg-CH_3) = 2.45 N cm^{-1}.

The IR and Raman spectra of $C(HgX)_4$ (X = Cl, Br, I, F) have been studied and discussed by German workers (97). Raycheba and Geier (82a) have reported Raman frequencies of the symmetric

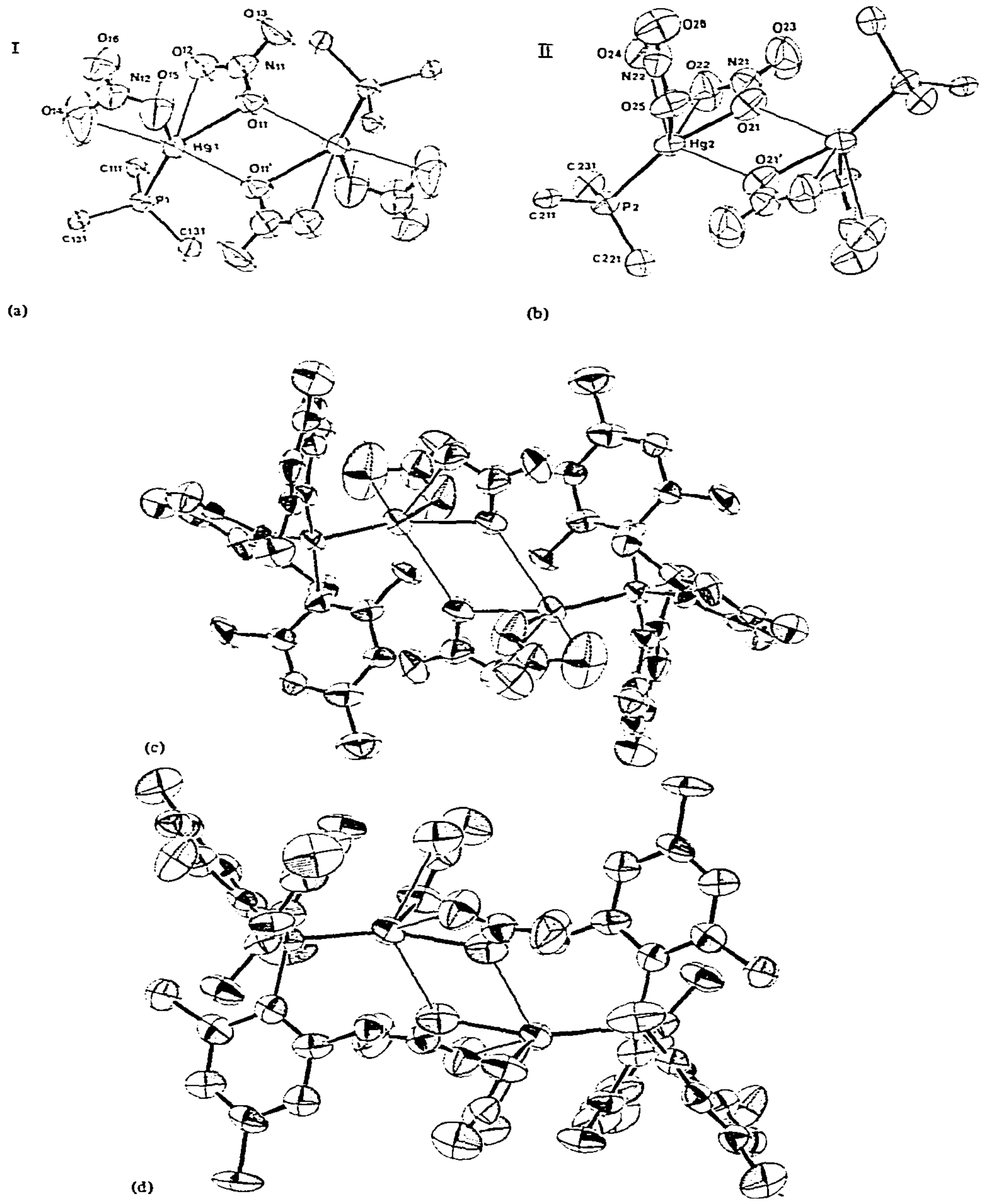

Figure 22. Views with 50% probability ellipsoids of (a) and (c) dimer I, and (b) and (d) dimer II, of [(mesityl)$_3$PHg-(NO$_3$)$_2$]$_2$ showing the molecular goemetry. Only the mesitylcarbon atoms bonded to phosphorus are shown in (a) and (b). From E. C. Alyea, S. A. Dias, G. Ferguson and M. Parvez, Inorg. Chim. Acta, 37 (1979) 45.

TABLE 17. Raman Frequencies of the Symmetric Methyl C-Hg Vibration in CH_3HgL Complexes (82a).

complex	$\bar{\nu}_{CH_3\text{-}Hg}$, cm^{-1}	donor atom
CH_3Hg meldrumate[b]	550	C
$CH_3HgCH(CN)_2$[c]	545[a]	C
$CH_3HgCH(CN)(SO_2C_6H_5)$[c]	545 (540)[a]	C
CH_3Hg dimethylbarbiturate[c]	543	C
CH_3Hg dimedonate[c]	540	C
CH_3Hg barbiturate[c]	570	O/N
CH_3HgCH_3[d]	550	C
CH_3HgCN[e]	564	C
$CH_3HgOH_2^+$[f]	570	O
CH_3HgOH[g]	577	O
CH_3HgONO_2[f]	566	O
$CH_3HgOSO_3^-$[h]	566	O
$CH_3HgNH_3^+$[i]	565	N

[a] IR, CsBr pellet. [b] Aqueous solution; 0.04 M, pH 4.7. [c] Solid sample. [d] K. Brodersen, Chem. Ber., 90, 2703 (1957). [e] P. L. Goggin and L. A. Woodward, Trans. Faraday Soc., 62, 1423 (1966). [f] P. L. Goggin and L. A. Woodward, ibid., 58, 1495 (1962). [g] P. L. Goggin and L. A. Woodward, ibid., 56, 1591 (1960). [h] J. H. R. Charke and L. A. Woodward, ibid., 64, 1041 (1968). [i] W. Beitelschmidt, Dissertation, Friedrich-Alexander-Universität, Erlangen-Nürnberg, 1972.

methyl C-Hg vibration in a number of CH_3HgL complexes containing C-, O- or N-donor L ligands (Table 17). It appears to be possible to distinguish between C- and O-coordination to $CH_3Hg(II)$: CH_3-Hg vibration = 580-565 cm^{-1} for O-coordination; 565-540 cm^{-1} for C-coordination.

The vibrational spectra of tertiary phosphine/Hg(II) complexes have been measured and evaluated (163).

B. Nuclear Magnetic Resonance Spectroscopy

A broadly ranging NMR study of some 2-coordinate Hg(II) compounds has compared the chemical shifts of ^{13}C, ^{19}F, ^{31}P and ^{199}Hg and spin-spin coupling constants of ^{1}H, ^{13}C, ^{19}F and ^{31}P to ^{199}Hg in complexes of type $[XHgPMe_3]^+$, CH_3HgX, CF_3HgX, XHgCN and PhHgX (X = Cl, Br, I, CH_3, CF_3, CCl_3, C_6H_5, CN, PMe_3^+) (164). Tables 18-27 present useful chemical shift and spin-spin coupling constant

TABLE 18.

Chemical shifts of ^{199}Hg and ^{13}C in some methyl mercury compounds (164)

Compound	Solvent	$\delta(^{199}Hg)^a$	$\delta(^{13}C)^b$
$Hg(CH_3)_2$	$CH_2Cl_2(CDCl_3)$	-46^c	$(23.4)^d$
$Hg(CH_3)(C_6H_5)$	$CDCl_3$	-392	14.5
$Hg(CH_3)(CF_3)$	CH_2Cl_2	-799	7.4
$[Hg(CH_3)PMe_3][NO_3]$	D_2O	-655	$(8.0)^e$
$Hg(CH_3)CN$	$CH_2Cl_2(thf)$	-692	$(3.1)^f$
$Hg(CH_3)I$	$CH_2Cl_2(CDCl_3)$	$-1\ 097^c$	$(18.8)^d$
$Hg(CH_3)Br$	$CH_2Cl_2(CDCl_3)$	-915^c	$(12.8)^d$
$Hg(CH_3)Cl$	$CH_2Cl_2(CDCl_3)$	-814^c	$(8.6)^d$

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[a] In p.p.m. to high frequency of neat $HgMe_2$. [b] In p.p.m. to high frequency of $SiMe_4$; CH_3 carbon. [c] P. L. Goggin, R. J. Goodfellow, and N. W. Hurst, J. C. S. Dalton, 1978, 561. [d] A. J. Brown, O. W. Howarth, and P. Moore, J. C. S. Dalton, 1976, 1589. [e] In 1:1 D_2O:-MeOH. [f] 20% $(CD_3)_2CO$ added.

TABLE 19.

Coupling constants (Hz) involving the methyl group in some of its mercury derivatives (164)

Compound	Solvent[a]	^1J(HgC)	^2J(HgH)
$Hg(CH_3)_2$	$(CD_3)_2SO$	726[a]	105.1[a]
$[Hg(CH_3)PMe_3][NO_3]$	D_2O	(1 256)[b]	166.6[c]
$Hg(CH_3)CN$	thf[d]	1 425[e]	174.0
$Hg(CH_3)I$	$(CD_3)_2SO$	1 540[a]	208[a]
$Hg(CH_3)Br$	$(CD_3)_2SO$	1 631[a]	217.7[a]
$Hg(CH_3)Cl$	$(CD_3)_2SO$	1 673[a]	221.5[a]
$Hg(CH_3)_2$[f]	$CDCl_3$	639[a]	102.0[g]
$Hg(CH_3)(C_6H_5)$	$CDCl_3$	760	110.4
$Hg(CH_3)(CF_3)$[f]	CH_2Cl_2	960	136.4
$Hg(CH_3)CN$	$CDCl_3$	1 326	171.6[h]
$Hg(CH_3)I$	$CDCl_3$	1 301[a]	184[a]
$Hg(CH_3)Br$	$CDCl_3$	1 395[a]	196.9[a]
$Hg(CH_3)Cl$	$CDCl_3$	1 431[a]	203.6[a]

[a] A. J. Brown, O. W. Howarth, and P. Moore, J.C.S. Dalton, 1976, 1589. [b] In 1:1 D_2O:MeOH; ^2J(PC), 78. [c] ^3J(PH), -7.1. [d] thf = tetrahydrofuran. [e] 20% $(CD_3)_2CO$ added. [f] See Table 1 for further details. [g] V. S. Petrosyan and O. A. Reutov, J. Organometal. Chem., 1974, 76, 123. [h] In CH_2Cl_2.

data. There appears to be no direct correlation between $\delta(^{199}Hg)$ and *trans* influences. An Australian group has reported a study of the ^1H and ^{199}Hg NMR spectra of some $CH_3Hg(II)$ complexes of type $[CH_3HgL]NO_3$ (L = substituted pyridine) (165). A direct correlation was found between $J(^1H-^{199}Hg)$ and the pK_a and the gas phase enthalpy of ionization of LH^+. The proton and ^{13}C NMR spectra of the methylmercuric halides, partially oriented in Merck Phase IV, have been obtained and evaluated (166). H-C-H Bond angles could be calculated.

TABLE 20.

Chemical shifts of ^{199}Hg, ^{19}F and ^{13}C in some trifluoromethylmercury compounds. (164)

Compound	Solvent	$\delta(^{199}Hg)^a$	$\delta(^{19}F)^b$	$\delta(^{13}C)^c$
$Hg(CF_3)_2$	thf	-1 675	-37.30	
$[Hg(CF_3)PMe_3][NO_3]$	Me_2SO	-1 405	-34.14	162.8
$Hg(CF_3)CN$	thf	-1 559	-35.95	156.5^d
$Hg(CF_3)I$	thf	-2 062	-34.38	157.7^d
$Hg(CF_3)Br$	thf	-1 791	-33.53	153.9^d
$Hg(CF_3)Cl$	thf	-1 638	-33.21	
$Hg(CF_3)(CH_3)$	CH_2Cl_2	-799	-38.57	183.2
$Hg(CF_3)(C_6H_5)$	$CDCl_3$	-1 160	-36.71	175.0
$Hg(CF_3)_2$	CH_2Cl_2	-1 611	-36.43	161.0
$Hg(CF_3)I$	$CH_2Cl_2(CDCl_3)$	-1 979	-33.38	(154.5)
$Hg(CF_3)Br$	$CH_2Cl_2(CDCl_3)$	-1 719	-32.42	(150.3)
$Hg(CF_3)Cl$	$CH_2Cl_2(CDCl_3)$	-1 578	-32.01	(147.7)

[a] In p.p.m. to high frequency of neat $HgMe_2$.

[b] In p.p.m. to high frequency of $CFCl_3$.

[c] In p.p.m. to high frequency of $SiMe_4$; CF_3 carbon.

[d] In 20% $(CD_3)_2CO$ added.

The proton NMR spectrum of allylmercuric chloride has been reinvestigated (57). In acetone-d_6 at -20°C the following spectrum was observed: δ 2.76 (d, 2H), 4.7 (t, 2H) and 5.72 ppm (complex m, 1H); $J(^1H-^{199}Hg)$ = 288 Hz. This is indicative of a stable σ-allyl form, $CH_2{=}CHCH_2HgCl$ and stands in contrast to previous studies (Kitching et al., J. Organometal. Chem., 34 (1972) 233) which reported rapid rearrangement on the NMR timescale. The culprit appears to be mercuric chloride, trace amounts of which catalyze this dynamic process, as control experiments showed. Figure 23 shows the proton NMR spectra of pure $CH_2{=}CHCH_2HgCl$ in acetone-d_6

TABLE 21.

Coupling constants (Hz) involving the trifluoromethyl group in some of its mercury derivatives. (164)

Compound	Solvent	$^1J(HgC)$	$^1J(FC)$	$^2J(HgF)$
$Hg(CF_3)_2$	thf			1 317.7
$[Hg(CF_3)PMe_3][NO_3]$	D_2O			1 452.6[a]
$[Hg(CF_3)PMe_3][NO_3]$	Me_2SO	3 676	363[b]	1 411.6[c]
$Hg(CF_3)CN$	thf	4 169[d]	351[d]	1 603.2
$Hg(CF_3)I$	thf			1 744.1
$Hg(CF_3)Br$	thf			1 862.2
$Hg(CF_3)Cl$	thf			1 912.6
$Hg(CF_3)CH_3$	CH_2Cl_2	1 735	360.2	936.6
$Hg(CF_3)C_6H_5$	CH_2Cl_2		359	1 006.8
$Hg(CF_3)_2$	CH_2Cl_2	2 993	355.3	1 263.6
$Hg(CF_3)I$	$CDCl_3(CH_2Cl_2)$	4 279		(1 700.8)
$Hg(CF_3)Br$	$CDCl_3(CH_2Cl_2)$	4 507	361	(1 840.9)
$Hg(CF_3)Cl$	$CDCl_3(CH_2Cl_2)$	4 643		(1 911.4)

[a] $^3J(PF)$, +43. [b] $^2J(PC)$, 154. [c] $^3J(PF)$, +40. [d] 20% $(CD_3)_2CO$ added.

at 25°C (A) and of a solution to which trace amounts of $HgCl_2$ have been added (B). Crotylmercuric chloride also showed a proton NMR spectrum indicative of the static σ-structure, $CH_3CH{=}CH{-}CH_2HgCl$.

The ^1H NMR spectra of $(CH_2{=}CH{-}C{\equiv}C)_2Hg$ and of 5-chloromercurithiophene-2-aldehyde, 61, have been measured, with particular interest in long-range $^1H-^{199}Hg$ spin-spin coupling (167). Also

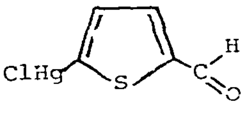

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TABLE 22.

Values and signs of spin-spin coupling constants in $Hg(CF_3)_2$, $Hg(CF_3)CH_3$ and $Hg(CH_3)_2$. (164)

	$Hg(CF_3)_2$[a]	$Hg(CF_3)CH_3$[a]	$Hg(CH_3)_2$[b]
$^1J(CH)$		+133.7	+129.6
$^1J(FC)$	−355.3	−360.2	
$^1J(HgC)(CH_3)$		960	+687
$^1J(HgC)(CF_3)$	+2 993	1 735	
$^2J(HgH)$		−136.4	−101.5
$^2J(HgF)$	+1 263.6	+936.6	
$^3J(CH)$		−3.6	−1.9
$^3J(FC)$	+24.5	+12.2	
$^4J(HH)$			+0.45
$^4J(FH)$		−0.5	
$^4J(FF)$	+4.9		

[a] in CH_2Cl_2. [b] neat liquid with 5% C_6H_6 added, R. R. Dean and W. McFarlane, Mol. Phys., 1967, 13, 343.

TABLE 23.

N.m.r. parameters of some trichloromethylmercury compounds. (164)

Compound	Solvent	$\delta(^{199}Hg)$[a]	$\delta(^{13}C)$[b]	$^1J(HgC)$/Hz
$Hg(CCl_3)_2$	thf (Me_2CO)	−1 863	(115.2)	(2 356)
$Hg(CCl_3)Br$	thf (Me_2CO)	−1 931	(112.3)	
$Hg(CCl_3)Cl$	thf (Me_2CO)	−1 746	(109.1)	(4 022)

[a] In p.p.m. to high frequency of neat $HgMe_2$. [b] In p.p.m. to high frequency of $SiMe_4$.

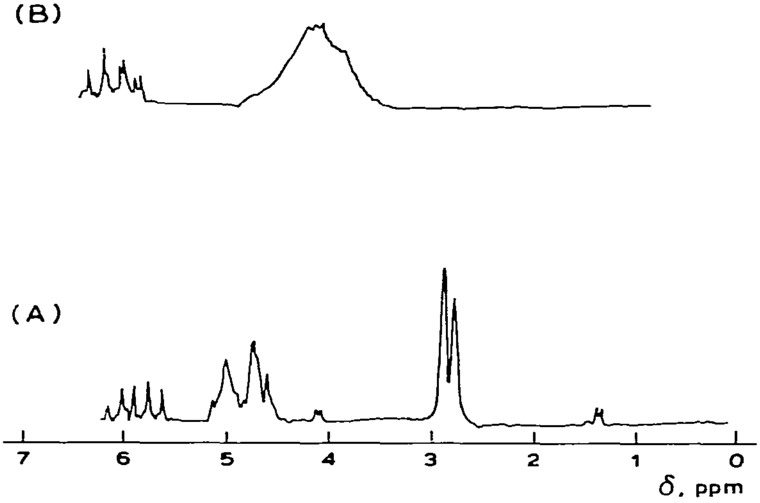

Figure 23. Proton NMR spectra of pure allylmercuric chloride in acetone-d_6 at 25°C (A) and of allylmercuric chloride containing a trace amount of mercuric chloride (same conditions) (B). From A. S. Ivanov and A. Z. Rubezhov, Izv. Akad. Nauk SSSR, Ser. Khim. (1979) 1349.

studied have been the ^{1}H and ^{13}C NMR spectra of bis(bicyclo[1.1.0]-but-1-yl)mercury (7) and the ^{1}H NMR spectra of *threo*- and *erythro*-PhCHDCHDHgCl (10).

Russian workers have reported a detailed study of the proton NMR spectra of a series of *para*-substituted arylmercuric chlorides and acetates, p-XC_6H_4HgY (Y = Cl, OAc; X = Me_2N, PhO, MeO, Me, H, F, Cl, CF_3, CO_2H, CO_2Et, NO_2) (168). Table 28 gives results. The effects of the X substituents on the shieldings of the aromatic ring protons in these mercurials were very similar to the effects

TABLE 24.

Some n.m.r. parameters of phenylmercury compounds. (164)

Compound	Solvent	δ(^{199}Hg)[a]	δ(^{13}C)[b,c]	^{1}J(HgC)/Hz[c]
$Hg(C_6H_5)(CH_3)$	$CDCl_3$	− 392	179.0	1 080[d]
$Hg(C_6H_5)_2$	$CDCl_3$	(− 745)[e]	170.4[f]	1 176[f]
	Me_2SO	− 808[g]	172.5[h]	1 275[h]
$Hg(C_6H_5)(CF_3)$	$CDCl_3$	−1 160	158.5[i]	
$[Hg(C_6H_5)PMe_3][NO_3]$	$MeNO_2$	−1 045		
$Hg(C_6H_5)CN$	Me_2SO	−1 119	(155.1)[j]	(2 156)[j]
$Hg(C_6H_5)I$	Me_2SO	−1 469		
$Hg(C_6H_5)Br$	Me_2SO	−1 287	156.4[h]	
$Hg(C_6H_5)Cl$	Me_2SO	−1 182	(150.5)[f,k]	(2 530)[f,k]

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[a] In p.p.m. to high frequency of neat $HgMe_2$.

[b] In p.p.m. to high frequency of $SiMe_4$.

[c] C_α of phenyl group.

[d] o-C, δ 136.9, ^{2}J(HgC) 84; m-C, δ 128.6, ^{3}J(HgC) 96; p-C, δ 127.7.

[e] In CH_2Cl_2, A.P. Tupčiauskas, N. M. Sergeyev, Yu. A. Ustynyuk, and A. N. Kashing, J. Magnetic Resonance, 1972, 7, 124.

[f] J. Browning, P. L. Goggin, R. J. Goodfellow, N. W. Hurst, L. G. Mallinson, and M. Murray, J.C.S. Dalton, 1978, 872.

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[h] A. J. Brown, O. W. Howarth, and P. Moore, J. C. S. Dalton, 1976, 1589.

[i] o-C, δ 137.7, ^{2}J(HgC) 93; m-C, δ 128.8, ^{3}J(HgC) 127; p-C, δ 128.3.

[j] In thf + 20% $(CD_3)_2CO$; o-C, δ 138.4, ^{2}J(HgC) 98; m-C, δ 128.9, ^{3}J(HgC) 163; p-C, δ 128.9.

[k] In dimethylformamide + $(CD_3)_2CO$ at 340K.

observed in the substituted benzenes, C_6H_5X:

$NO_2 < H, Cl < F, CH_3 < OMe < NMe_2$

$\longrightarrow$ increased shielding of the protons *ortho* to X

Two groups have reported ^{199}Hg chemical shifts and $^1H-^{199}Hg$ spin-spin coupling constants for some Group IV mercurials: $(Me_3C)_2Hg$, $(Me_3Si)_2Hg$, $(t\text{-}BuMe_2Si)_2Hg$, $(Me_3Ge)_2Hg$ and $[(Me_3SiCH_2)_3Sn]_2Hg$ (169) and $(Et_3Ge)_2Hg$ (170). Of particular interest is the large magnitude of the downfield shift of ^{199}Hg in the spectra of those compounds containing Hg-Si, Hg-Ge and Hg-Sn bonds.

TABLE 25.

N.m.r. parameters of some cyanomercury compounds. (164)

Compound	Solvent	$\delta(^{199}Hg)$[a]	$\delta(^{13}C)$[b,c]	$^1J(HgC)/Hz$[c]
$HgCN(CH_3)$	thf	- 766	165.9[d]	1 163[d,e]
$HgCN(C_6H_5)$	thf		159.0[d]	1 373[d]
$HgCN(CF_3)$	thf	-1 559	147.2[d]	2 094[d,f]
$Hg(CN)_2$	thf	-1 386	142.7[d]	3 037[d]
$Hg(CN)I$	thf	-1 942	146.0[d]	
$Hg(CN)Br$	thf	-1 615	140.8[d]	3 430[d]
$Hg(CN)Cl$	thf	-1 434	137.6[d]	3 610[d]
$HgCN(C_6H_5)$	Me_2SO	-1 119		
$[HgCN(PMe_3)][BF_4]$	Me_2SO	-1 240	151.3[g]	
$Hg(CN)_2$	Me_2SO		144.2	3 142

---

[a] In p.p.m. to high frequency of neat $HgMe_2$.

[b] In p.p.m. to high frequency of $SiMe_4$.

[c] CN carbon.

[d] 20% $(CD_3)_2CO$ added.

[e] 1 021 Hz in $CDCl_3$.

[f] $^3J(FC)$ = 14 Hz.

[g] $^2J(PC)$ = 95 Hz.

TABLE 26.

Chemical shifts of ^{199}Hg, ^{31}P and ^{1}H in some complex trimethylphosphine mercury cations. (164)

Compound	Solvent	$\delta(^{199}Hg)^a$	$\delta(^{31}P)^b$	$\delta(^{1}H)^c$
$[Hg(C_6H_5)PMe_3][NO_3]$	$MeNO_2$	-1 045	23.1	1.83
$[HgCl(PMe_3)][BF_4]$	$MeNO_2$	-1 353	18.5	2.06
$[Hg(CH_3)PMe_3][NO_3]^d$	D_2O	-655	29.8	1.73
$[Hg(CF_3)PMe_3][NO_3]$	D_2O	-1 433	10.0	1.81
$[Hg(PMe_3)_2][BF_4]_2$	D_2O	-1 159	18.8	1.86
$[Hg(CN)PMe_3][BF_4]$	D_2O	-1 267	8.5	1.83
$[HgI(PMe_3)][BF_4]$	D_2O	-1 856	18.8	1.86
$[HgBr(PMe_3)][BF_4]$	D_2O	-1 490	16.3	1.90
$[HgCl(PMe_3)][BF_4]$	D_2O	-1 299	13.9	1.91
$[Hg(CF_3)PMe_3][NO_3]^e$	Me_2SO	-1 405	10.7	1.68
$[Hg(CCl_3)PMe_3][NO_3]$	Me_2SO	-1 514	14.2	1.72
$[Hg(PMe_3)_2][NO_3]$	Me_2SO	-1 134	17.4	1.76
$[Hg(CN)PMe_3][BF_4]^f$	Me_2SO	-1 240	10.5	1.69
$[HgI(PMe_3)][NO_3]$	Me_2SO	-1 773	18.3	1.74
$[HgBr(PMe_3)][NO_3]$	Me_2SO	-1 442	17.4	1.76
$[HgCl(PMe_3)][NO_3]$	Me_2SO	-1 252	15.4	1.77

[a] In p.p.m. to high frequency of neat $HgMe_2$. [b] In p.p.m. to high frequency of 85% H_3PO_4. [c] PMe_3 protons.
For PMe_3 group $\delta(^{13}C)$ is [d] 10.1 in 1:1 D_2O-MeOH; [e] 11.5 and [f] 11.3 p.p.m.

Studies of the ^{199}Hg NMR spectra of $Hg[M(CO)_3Cp]_2$ and $CpM(CO)_3HgCl$ (M = Cr, Mo, W) and of $CpW(CO)_3HgX$ (X = Cl, Br, I, SCN), as well as of Et_2Hg, (171) and of ^{19}F NMR spectra of fluorobenzoates, $R_nMO_2CC_6H_4F$-p, including $PhHgO_2CC_6H_4F$-p, (172) have been reported.

TABLE 27.

Coupling constants (Hz) involving the trimethylphosphine ligand in some mercury complex cations. (164)

Complex	Solvent	^1J(HgP)	^2J(PH)	^3J(HgH)
$[Hg(C_6H_5)PMe_3][NO_3]$	$MeNO_2$	+2 641	−12.5	+50.8
$[HgCl(PMe_3)][NO_3]$	$MeNO_2$	+6 947	−14.0	+120.2
$[Hg(CH_3)PMe_3][NO_3]$[a]	D_2O	+1 768	−12.4	+44.6
$[Hg(CF_3)PMe_3][NO_3]$	D_2O	+4 371	−13.1	+72.9
$[Hg(PMe_3)_2][BF_4]_2$	D_2O	+5 173	(−10.6)[b,c]	+84.3
$[Hg(CN)PMe_3][BF_4]$	D_2O	+6 966	−13.6	+99.6
$[HgI(PMe_3)][BF_4]$	D_2O	+6 357	−13.7	+106.4
$[HgBr(PMe_3)][BF_4]$	D_2O	+7 308	−13.7	+117.0
$[HgCl(PMe_3)][BF_4]$	D_2O	+7 852	−13.8	+121.9
$[Hg(CF_3)PMe_3][NO_3]$[d]	Me_2SO	+5 226	−13.5	+73.9
$[Hg(CCl_3)PMe_3][NO_3]$	Me_2SO	+5 448	−13.6	+81.4
$[Hg(PMe_3)_2][BF_4]_2$	Me_2SO	+5 649	(−8.8)[b,e]	+81.3
$[Hg(CN)PMe_3][BF_4]$[f]	Me_2SO	+7 474	−13.5	+94.2
$[HgI(PMe_3)][NO_3]$	Me_2SO	+7 387	−13.9	+107.4
$[HgBr(PMe_3)][NO_3]$	Me_2SO	+8 143	−14.0	+115.2
$[HgCl(PMe_3)][NO_3]$	Me_2SO	+8 611	−14.1	+118.0

[a] ^1J(PC), 34; ^2J(HgC), 44 in 1:1 D_2O-MeOH. [b] $[^2J(PH) + {}^4J(PH)]$. [c] ^2J(PP) +250. [d] ^1J(PC), 36; ^1J(CH), 133; ^2J(HgC), 66. [e] ^2J(PP), +250. [f] ^1J(PC), 37; ^2J(HgC), 79.

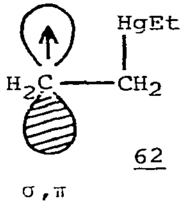
C. Electron Spin Resonance Spectroscopy

Radicals which were generated by exposure of diethylmercury, neat or in tetramethylsilane solution, to ^{60}Co γ-rays at 77°K included the species: $EtHgCH_2CH_2\bullet$ and $Et\bullet$, as well as the radical anion $[EtHgEt]^{\overline{\bullet}}$. These were detected and studied by ESR (173). Although structure 62 was favored for $EtHgCH_2CH_2\bullet$, 63 could not be excluded.

TABLE 28. Proton Chemical Shifts and Spin-Spin Coupling Constants in *para*-substituted Arylmercury Compounds, XC_6H_4HgY (168).

X	Y=Cl					Y=COCCH$_3$				
	δ_{H_2}, ppm relative to TMS	$J(^{199}Hg-H_2)$ Hz	δ_{H_3}, ppm relative to TMS	$J(^{199}Hg-H_3)$ Hz	$J(H_2-H_3)$ Hz	δ_{H_2}, ppm relative to TMS	$J(^{199}Hg-H_2)$ Hz	δ_{H_3}, ppm relative to TMS	$J(^{199}Hg-H_2)$ Hz	$J(H_2-H_3)$ Hz
$N(CH_3)_2$	7.23	192	6.66	--	--	7.12	194	6.62	36	7.5
OC_6H_5	7.46	193	--	--	8.1	--	--	--	--	--
OCH_3	7.37	192	6.90	42	--	7.29	194	6.87	39	7.6
CH_3	7.32	200	7.10	52	8.0	7.23	199	7.07	49	7.5
F	7.49	195	7.13	37	--	7.43	194	7.11	35	--
H	7.41	201	7.24	56	7.4	7.37	202	7.27	54	7.3
Cl	7.49	195	7.33	43		7.37	195	7.27	42	8.0

CF_3	7.71	196	7.60	43		--	--	--	--	--
COOH	7.61	195	7.90	50	7.8	--	--	--		--
$COOC_2H_5$	7.63	194	7.88	49	7.8	--	--	--	--	--
NO_2	7.76	189	8.10	39	8.1	7.71	191	8.11	26	8.2



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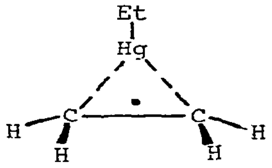

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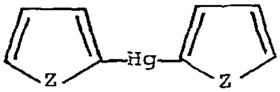
D. Photoelectron Spectroscopy

The UV and X-ray photoelectron spectra of several furyl- and thienylmercurials have been measured (174):



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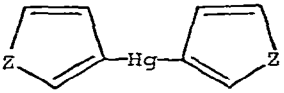

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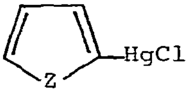

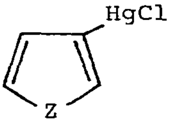

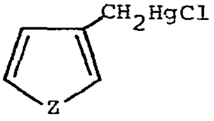

(Z = O and S)

In 64 and 65 there is a small charge-transfer interaction between the filled ring π orbitals and the vacant 6pπ mercury atomic orbitals. The involvement of mercury 5d orbitals in bonding is rather small.

E. Mass Spectroscopy

Negative ion mass spectroscopy has been used, with good success, to study the effects of σ,π conjugation in some organomercurials (175). This technique could distinguish between Series A and B in Table 11.

11. ANALYTICAL ASPECTS OF ORGANOMERCURY CHEMISTRY.

Papers on the following topics are noted:

- A method for the preconcentration of Hg(II) and $CH_3Hg(II)$ cations from aqueous solution which involved collection of these species on dithizone-coated macroreticular resin beads. Analysis is then accomplished using cold vapor atomic absorption spectrometry (176).

- The high-efficiency adsorption (Langmuir-type) of Hg(II) on several kinds of styrene-divinylbenzene copolymer beads from aqueous solutions over a wide range of pH. Chloride ion strongly reduced the adsorption and over 95% of the adsorbed Hg(II) could be washed from the resin with dilute HCl (177).
- Destruction of RHg(II) to give Hg(II) by BrO_3^-/Br^- in aqueous medium before determination of total mercury (178).
- Destruction of RHg(II) in aqueous solution by UV digestion before determination of total mercury by cold vapor atomic absorption spectrometry (179).
- Selective atomic absorption determination of Hg(II) and RHg(II) by combined use of Fe(III) and sodium borohydride (180).
- Simultaneous determination of oxygen and mercury in inorganic and organic mercury compounds (181).
- Determination of RHg(II) in fish tissue with an atomic absorption spectrometer used as a specific gas chromatography detector (182).
- Determination of $CH_3Hg(II)$ in fish by graphite furnace atomic absorption spectrometry (183).

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