MERCURY

ANNUAL SURVEY COVERING THE YEAR 1978

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Mercury; Annual Survey covering the year 1977 see J. Organometal. Chem., Vol. 176 (1979) p. 137–244.

1. REVIEWS AND BOOKS

A book by J.K. Kochi which deals with organometallic mechanisms covers a good deal of the mechanistic aspects of organomercurial reactions (1).

Reviews covering the following topics of organomercury chemistry have appeared:

- the use of organomercurials in organic synthesis (2);
- organomercurial reaction mechanisms (3,4);
- the aqueous solution chemistry of $CH_3Hg(II)$ and its complexes (5);
- the chemistry of $CH_3Hg(II)$ toxicology (6).

An American Chemical Society Symposium Series volume on the occurence and fate in the environment of organometals and organometalloids (7) contains the following (usually brief) reviews on topics in organomercury chemistry:

- kinetics and mechanim studies of B_{12}-dependent methyl transfer to mercury (Y.-T. Fanchiang, W.P. Riddley and J.M. Wood, p. 54);
- chemistry of organometallic cations (including RHg^+) in aqueous medium (R.S. Tobias, p. 13);
- organosilanes as alkylating agents for Hg(II) (R.E. De Simone, p. 149);
- transmethylation between aquated metal ions, including Hg(II) (K.L. Jewett, F.E. Brinckman and J.M. Bellama, p. 158);
- mechanisms for alkyl transfers in organometals (J.K. Kochi, p. 205);

- aspects of Hg(II) thiolate chemistry and the biological behavior of organomercury compounds (A.J. Canty, p. 327);
- mercury, lead and cadmium complexation by SH-containing amino acids (A.J. Carty, p. 339).

2. PREPARATION OF ORGANOMERCURY COMPOUNDS

A. Organometallic Routes

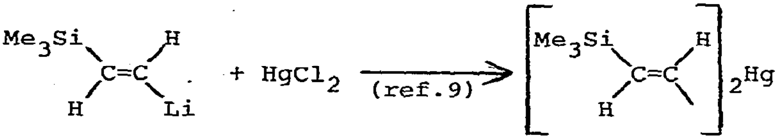
The synthesis of organomercurials by the organolithium and Grignard routes is routine. Interesting mercurials have been prepared using organolithium reagents:

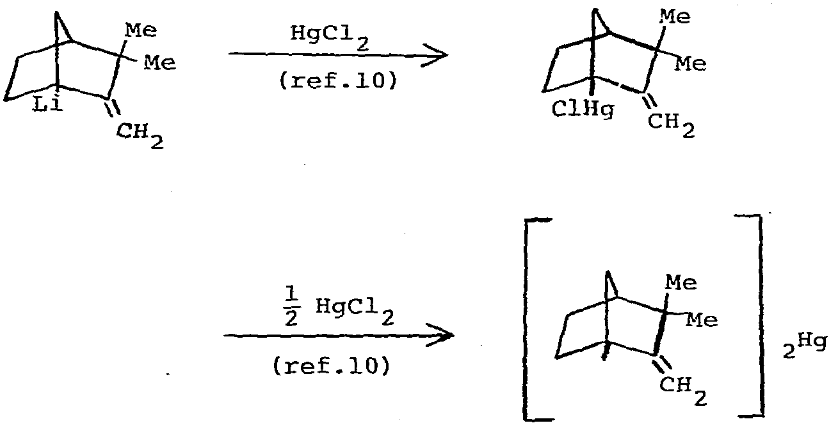
$$2\ (Me_3Si)_2CHLi + HgCl_2 \xrightarrow[\text{(ref.8)}]{} [(Me_3Si)_2CH]_2Hg$$

$$[(Me_3Si)_2CH]_2Hg + HgX_2 \longrightarrow 2(Me_3Si)_2CHHgX \qquad (X = Br,I)$$

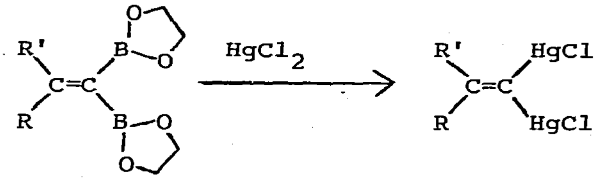
$$+ BCl_3 \longrightarrow (Me_3Si)_2CHHgCl$$

$$2\ (Me_3Si)_2(Me)CLi + HgCl_2 \xrightarrow[\text{(ref.8)}]{} [(Me_3Si)_2(Me)]_2Hg$$





1,1-Bis(trimethylenedioxyboryl)alkanes have been used to prepare 1,1-bis(chloromercuri)-1-alkenes (11):

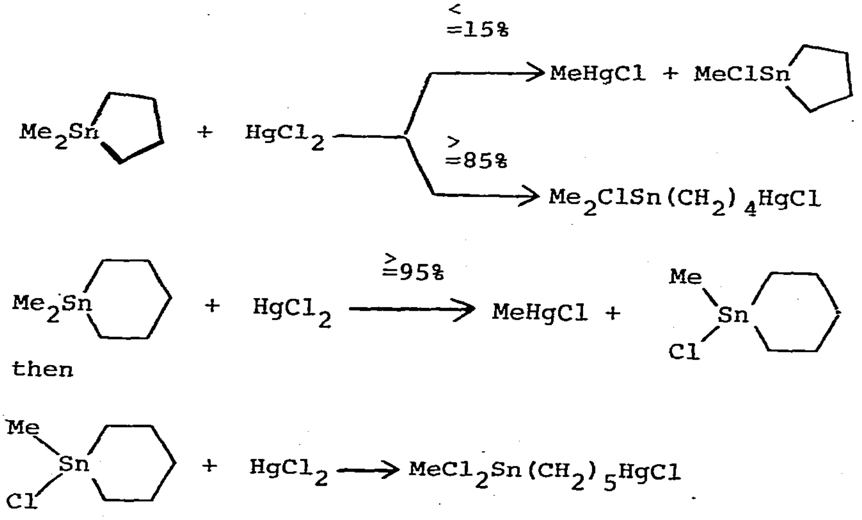


Prepared in this manner were $CH_2{=}C(HgCl)_2$ (70%), $Et_2CHCH{=}C(HgCl)_2$ (81%), $PhCH{=}C(HgCl)_2$ (85%), $Me_2C{=}C(HgCl)_2$ (85%), $[EtOC(O)](Me)C{=}C(HgCl)_2$ (80%), $Me_2C{=}CHC(Me){=}C(HgCl)_2$ (74%) and $(CH_2)_5C{=}C(HgCl)_2$ (97%).

Thallium reagents have been used to prepare bis(pentachlorophenyl)mercury (12):

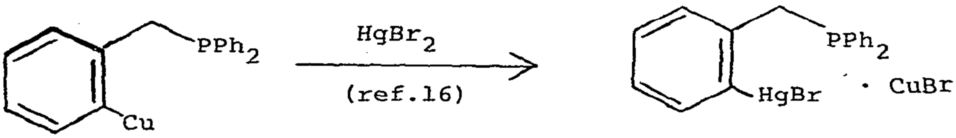
$$(C_6Cl_5)_2TlCl + Hg_2Cl_2 \longrightarrow (C_6Cl_5)_2Hg \quad (50\%)$$

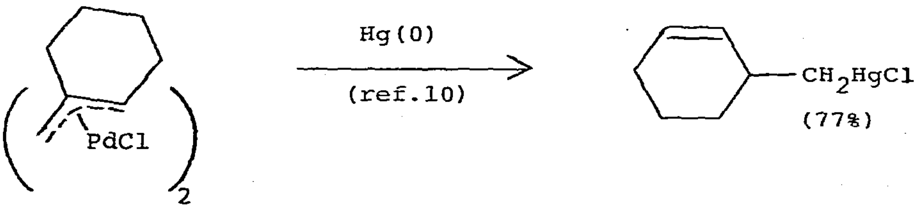
New examples of the transfer of organic substituents from Group IV organometallics to mercury have been recorded. The cleavage of methyl groups from methylsiloxanes by mercuric nitrate (13) is not of preparative value. The action of mercuric chloride on cyclic stannanes showed an interesting difference in chemioselectivity between a stannacyclopentane and a stannacyclohexane (14):

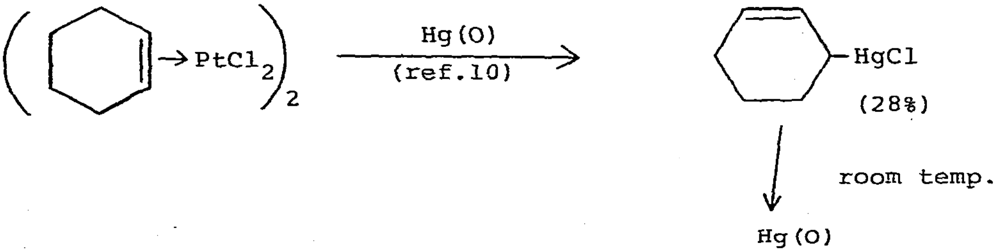


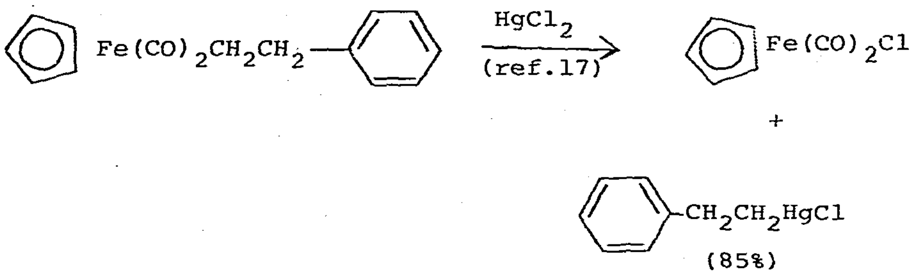
The kinetics of the cleavage of the phenyl-tin bond in triethylphenyltin by mercuric salts in methanol have been studied (15). The reactivity of the Hg(II) species investigated increased in the order HgI_3^- >>HgI_2>$HgCl_2$>$Hg(OAc)_2$. Phenyl cleavage from tin by HgX_2 is about 400 times faster than methyl cleavage. A mechanism involving an intermediate π-complex and a transition state that is not particularly polar was suggested.

Arylation or alkylation of Hg(II) halides by organotransition metal compounds occurs readily. Most of the examples reported are not of preparative utility, but some few are.

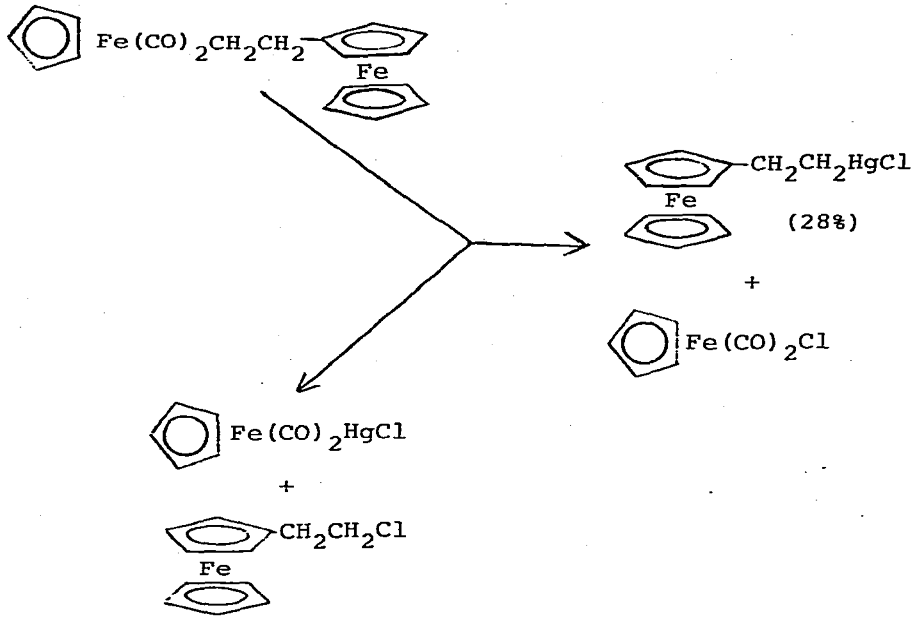








but:



Also studied have been the kinetics and mechanism of the methylation of mercuric chloride by methylcobalamin (18). The transfer of the methyl group as the carbanion is involved.

B. Electrochemical Procedures

The electrolysis of Na[CH_3AlCl_3] (1.2V, 1 amp, 216 hr.) using a mercury anode gave dimethylmercury (19). However, the conversion of the melt was only 28% and the current yield only 25%. Apparently the back-reaction between metallic aluminum at the cathode and dimethylmercury regenerates methylaluminum compounds. A French group has prepared 4-H-octafluorobutylmercury compounds by an electroreductive technique (20):

$$I(CF_2)_4I \xrightarrow[0.15\underline{M}\ LiClO_4]{\text{Hg cathode, DMF}} Hg(CF_2CF_2CF_2CF_2H)_2$$

While bis(octafluorobutyl)mercury was the only product isolated upon completion of the electrolysis, $H(CF_2)_4HgI$ was shown to be an intermediate product. Only small amounts of bis(1-norbornyl)mercury were found in the controlled potential electrolysis of 1-iodo- and 1-bromonorbornane at mercury pool cathodes in DMF containing $R_4N^+ClO_4^-$; norbornane is the principal product instead (21). This contrasts with the behavior of decyl iodide in similar electrolyses, in which di-*n*-decylmercury is formed in substantial quantity. This difference is explained in terms of the more facile reduction of the norbornyl radical to the anion, whose protonation gives the hydrocarbon.

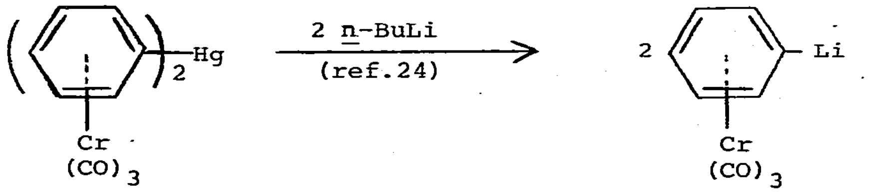
C. Miscellaneous

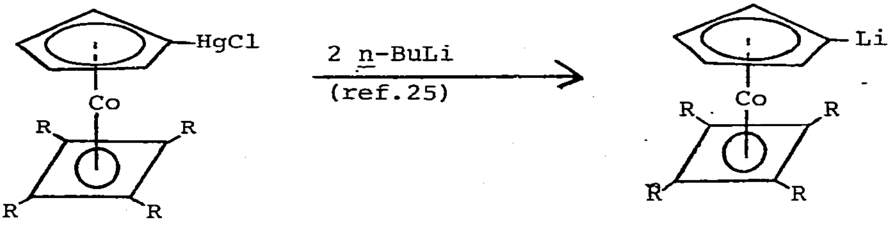
Since some organomercurial syntheses are based on reactions of elemental mercury, the generation and utilization of ultrasonically dispersed mercury should be of interest (22,23).

3. THE USE OF ORGANOMERCURY COMPOUNDS IN SYNTHESIS

A. Synthesis of Organometallic Compounds

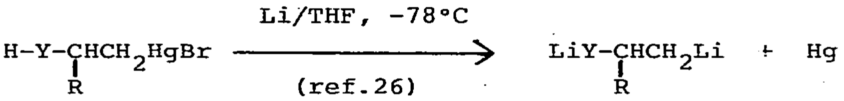
New examples of the synthesis of organolithium reagents from organomercurials have been reported.





(R = C_6H_5)

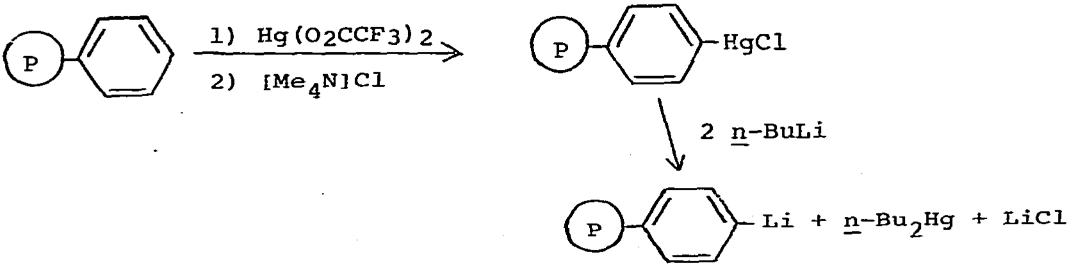
+ *n*-Bu_2Hg + LiCl



$$\text{H-Y-}\underset{\displaystyle R}{\text{CH}}\text{CH}_2\text{HgBr} \xrightarrow[\text{(ref.26)}]{\text{Li/THF, }-78\,^\circ\text{C}} \text{LiY-}\underset{\displaystyle R}{\text{CH}}\text{CH}_2\text{Li} + \text{Hg}$$

(Y = PhN, R = H
Y = PhN, R = Ph
Y = O, R = Ph)

Of particular interest are lithiated macroreticular copolymers of styrene and divinylbenzene which were prepared by an organomercury route (27):



The reaction of $(Me_3SiCH_2)_2Hg$ with metallic zinc gave $(Me_3SiCH_2)_2Zn$ (28) and cyclopentadienyldimethylborane has been prepared using dicyclopentadienylmercury (29):

$$(C_5H_5)_2Hg \quad + \quad Me_2BCl \longrightarrow Me_2BC_5H_5 \quad + \quad C_5H_5HgCl$$

Several examples of the use of organomercury compounds in the preparation of organometallic compounds of the Group IV elements are found in the 1978 literature:

$$Ph_2Hg \quad + \quad (Me_3Sn)_2S \xrightarrow[80°]{HMPA} HgS \quad + \quad 2\ Me_3SnPh \qquad \text{(ref.30)}$$

Bis(trifluoromethyl)mercury is a useful reagent for the preparation of CF_3-Ge and CF_3-Sn compounds (31):

$$(CF_3)_2Hg \quad + \quad GeBr_4 \xrightarrow{110°,\ 18\ hr} \underset{(55\%)}{CF_3GeBr_3} \quad + \quad \underset{(22\%)}{(CF_3)_2GeBr_2}$$

$$+ \quad \underset{(18\%)}{(CF_3)_3GeBr} \quad + \quad \underset{(4\%)}{(CF_3)_4Ge}$$

$$(CF_3)_2Hg + GeBr_4 \xrightarrow{150°,\ 24\ hr} \underset{(10\%)}{(CF_3)_2GeBr_2} \quad + \quad \underset{(65\%)}{(CF_3)_3GeBr}$$

$$+ \ \underset{(20\%)}{(CF_3)_4Ge}$$

$$(CF_3)_2Hg + GeI_4 \xrightarrow{120^\circ,\ 120\ hr} (CF_3)_4GeI_{4-n}$$

In the last reaction, the yields of the various products depended on the ratio of the reactants used. An about 2:1 $(CF_3)_2Hg/GeI_4$ ratio gave $(CF_3)_3GeI$ (72%) and $(CF_3)_4Ge$ (15%), while a 1:2 ratio gave CF_3GeI_3 (90%). $(CF_3)_2GeI_2$ was the predominant product when the $(CF_3)_2Hg/GeI_4$ ratio used was 1.72.

$$(C_2F_5)_2Hg + GeI_4 \xrightarrow{135^\circ,\ 21\ d} C_2F_5GeI_3 \qquad (53\%)$$

$$(CF_3)_2Hg + SnBr_4 \xrightarrow{25^\circ} (CF_3)_4SnBr_{4-n}$$

Here also the reactant ratio determined which products predominated. Isolated and characterized were CF_3SnBr_3 and $(CF_3)_2SnBr_2$. Reactions of bis(trifluoromethyl)mercury with $SiCl_4$, $SiBr_4$ and SiI_4 also were investigated (reaction temperatures 0-100°C), but no stable CF_3-Si derivatives were detected.

Bis(trifluoromethyl)mercury also undergoes CF_3-for-CH_3 displacement reactions with tetramethyltin, trimethyl(trifluoromethyl)tin and, most rapidly, with tetramethyllead (32):

$$\underset{\text{(excess)}}{(CF_3)_2Hg} + Me_4Pb \xrightarrow{70^\circ,\ 2\ weeks} Me_3PbCF_3 + MeHgCF_3 + Me_2Hg$$

$$(CF_3)_2Hg + Me_4Sn \xrightarrow{80^\circ,\ 2\ weeks} Me_3SnCF_3 + MeHgCF_3 + Me_2Hg$$

$$(CF_3)_2Hg + Me_3SnSnMe_3 \xrightarrow{75^\circ,\ 1\ week} Me_3SnCF_3 + Me_2Sn(CF_3)_2 + Me_4Sn + Hg$$

Organomercurials also have found useful application in the synthesis of σ- and π-bonded organic derivatives of the transition metals.

Nesmeyanov et al. have prepared σ-bonded organogold complexes using organomercury reagents (33):

$$R_2Hg + CH_3AuPPh_3 \longrightarrow [R(AuPPh_3)_2]BF_4$$

($R = XC_5H_4FeC_5H_4-$, with X = H, Cl, OMe and CO_2Me;

$R = YC_6H_4-$, with Y = H, Me, NH_2;

R = duryl, β-naphthyl, α-thienyl, styryl, $(OC)_3MnC_5H_4-$)

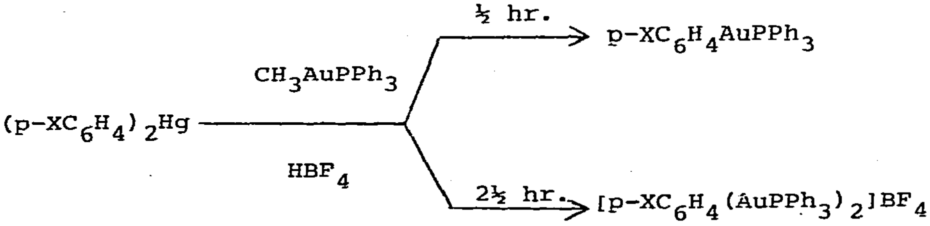
but:

$$R_2Hg + CH_3AuPPh_3 \xrightarrow{HBF_4} RAuPPh_3$$

($R = YC_6H_4-$, with Y = p- and m-CO_2Et;

$R = PhCH{=}\underset{|}{C}CO_2Et$)

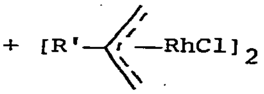
and:

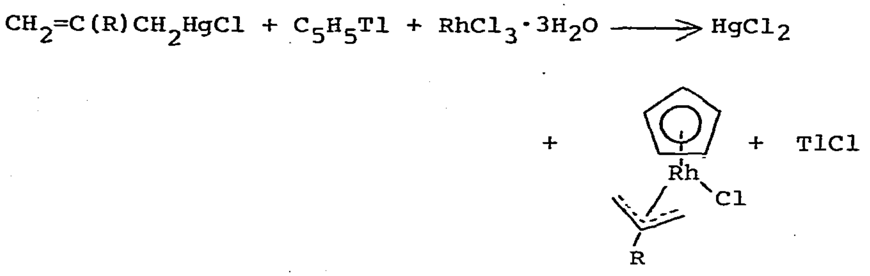


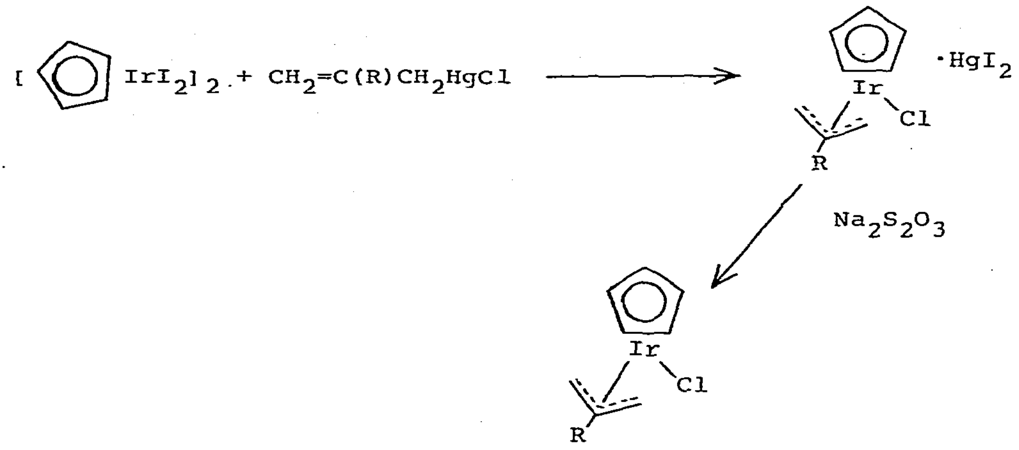
The reactive intermediate in these reactions was suggested and confirmed experimentally to be $[AuPPh_3]^+$, formed by the action of HBF_4 on CH_3AuPPh_3.

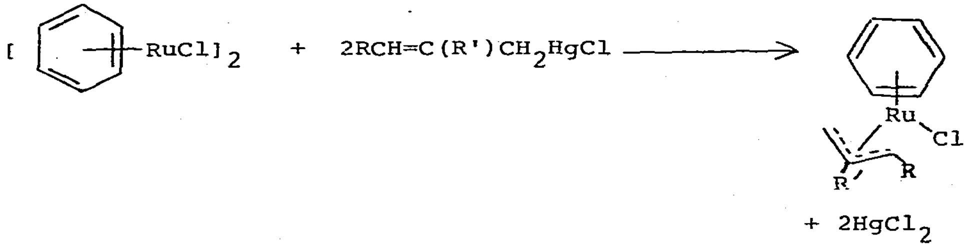
Allylic mercurials are known through the work of Nesmeyanov and Rubezhov to be excellent reagents for the synthesis of allyl derivatives of the Group VIII metals. These authors have now provided full details of this work (34), which was summarized previously in a series of preliminary communications reported in previous organomercury Annual Surveys. The equations which follow show some of the applications of allylmercury compounds which they describe.

$$4\ RCH{=}C(R')CH_2HgCl + 2\ Na_3RhCl_6 \longrightarrow 4\ HgCl_2 + 6\ NaCl$$

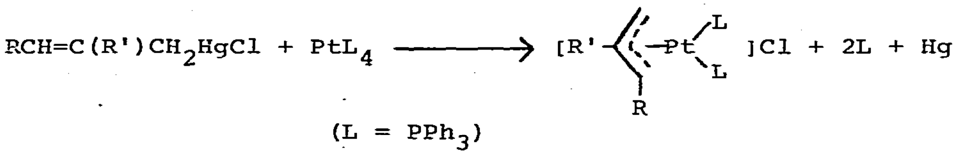




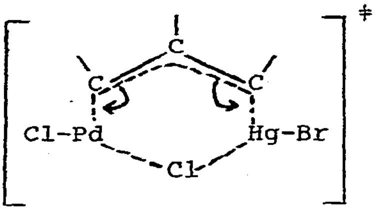




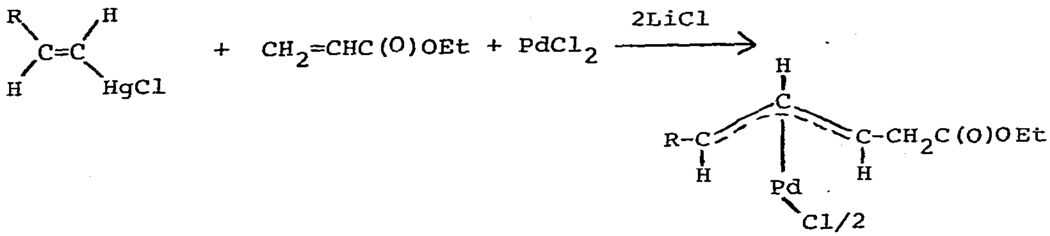
The same type of product was formed with $[(\pi\text{-}C_6H_6)OsCl_2]_2$.



The following transition state was suggested for the K_2PdCl_4/$CH_2{=}CHCH_2HgBr$ reaction, which gives the π-allylpalladium chloride dimer:



Larock and Mitchell have described a mercurial-based route to functionally substituted π-allylpalladium complexes (35):



The best yields were obtained when a ten-fold excess of the olefin and two equivalents of anhydrous lithium chloride in THF were allowed to react with the vinylic mercurial and palladium(II) chloride at 0°C. This reaction is generally applicable to the synthesis of π-allyl palladium complexes, as Table 1 shows.

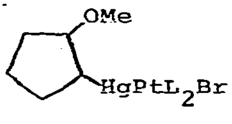
A number of papers has dealt with syntheses of organoplatinum complexes using organomercury reagents.

$Me_2Pt(bipy) + MeHgCl \longrightarrow fac\text{-}\ Me_3PtCl(bipy) + Hg$ (ref.36)

$(cycloalkyl)HgBr + PtL_3 \longrightarrow (cycloalkyl)Hg\text{-}PtL_2Br$ (ref.37)

$(L = PPh_3)$

The products of these reactions underwent demercuration upon exposure to sunlight, giving (cycloalkyl)PtL_2Br. The following compounds were thus prepared:



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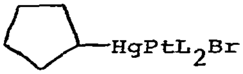

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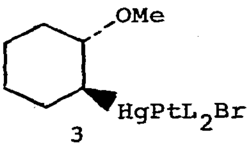

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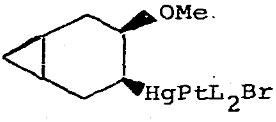

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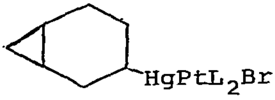

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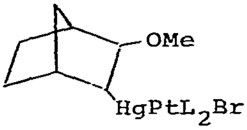

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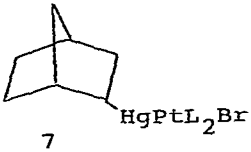

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(L = PPh_3)

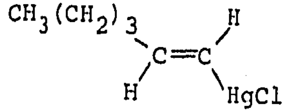
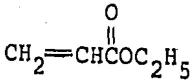
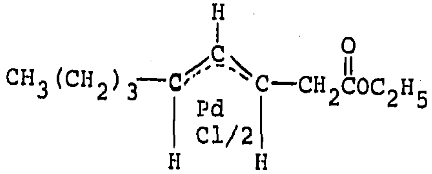
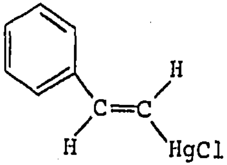
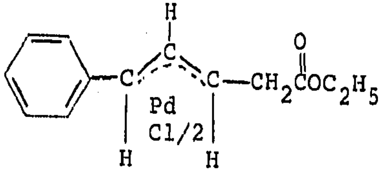
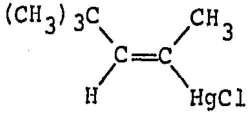
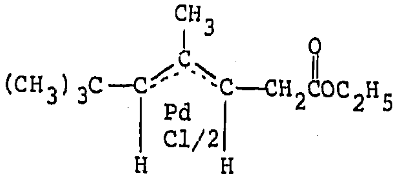
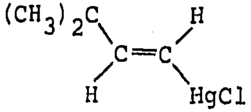
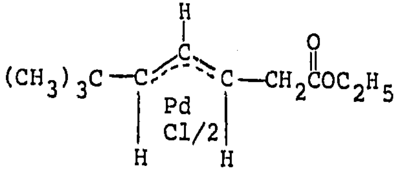
The stability of these compounds toward photolytic demercuration increased in order 1<2<3<4<5<6<7. It must be noted that the alternative structure, BrHgPt(cycloalkyl)L_2, was not excluded.

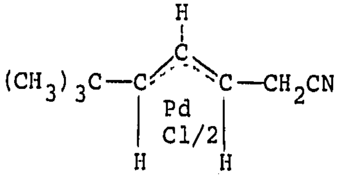
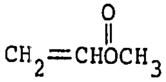
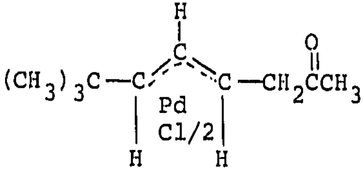
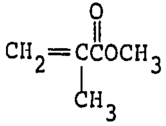
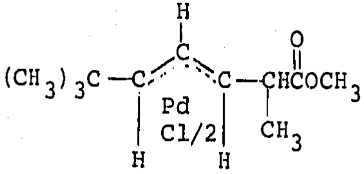
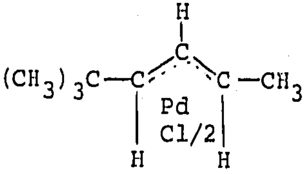
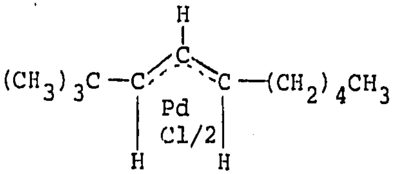
This reaction also has been carried out with the diastereoisomeric L-menthyl esters of α-bromomercuriphenylacetic acid (38). Optically active platinum-mercury complexes were obtained, and it was concluded that the main process which occurs is L_2Pt insertion into the Hg-Br bond to give $PhCH(CO_2C_{10}H_{19})HgPtL_2Br$. A lesser pathway involves stereoselective L_2Pt insertion into the Hg-C bond. Detailed mechanistic discussions are given and parallels to the R_2Hg/Hg reaction are drawn.

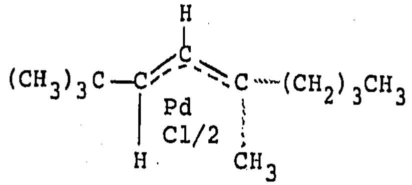
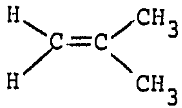
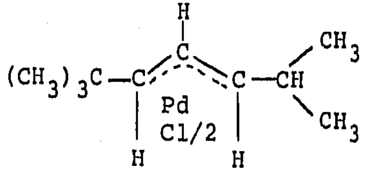
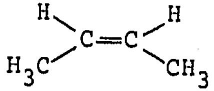
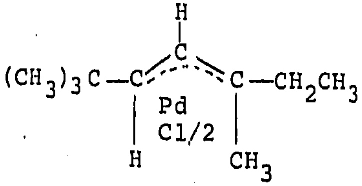
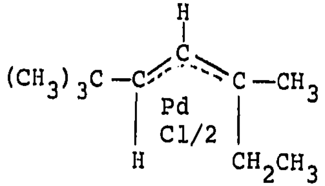
Such PtL_2 insertion into an olefin aminomercuration

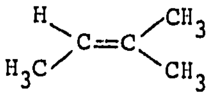
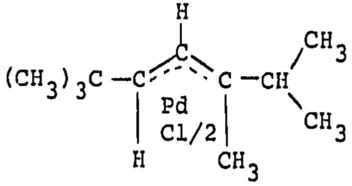
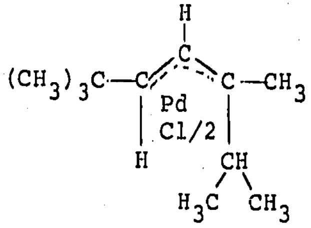
(Continued on p.158)

TABLE 1. Synthesis of π-Allylpalladium Complexes (35)[a]

Vinylmercuric chloride	Alkene	π-Allylpalladium compd	% Yield[b]
	 $CH_2{=}CH\overset{O}{\overset{\|}{C}}OC_2H_5$		66
			100(58)
			97(83)
			90(82)

$CH_2{=}CHCN$		87(71)
 $CH_2{=}CH\overset{\overset{O}{\parallel}}{O}CH_3$		100(67)
 $CH_2{=}\underset{CH_3}{\underset{\mid}{C}}\overset{\overset{O}{\parallel}}{C}OCH_3$		29(22)
$CH_2{=}CH_2$		92
$CH_2{=}CH(CH_2)_3CH_3$		67(63)

		
		41(21)
		59(37)
		

	 	19(7)

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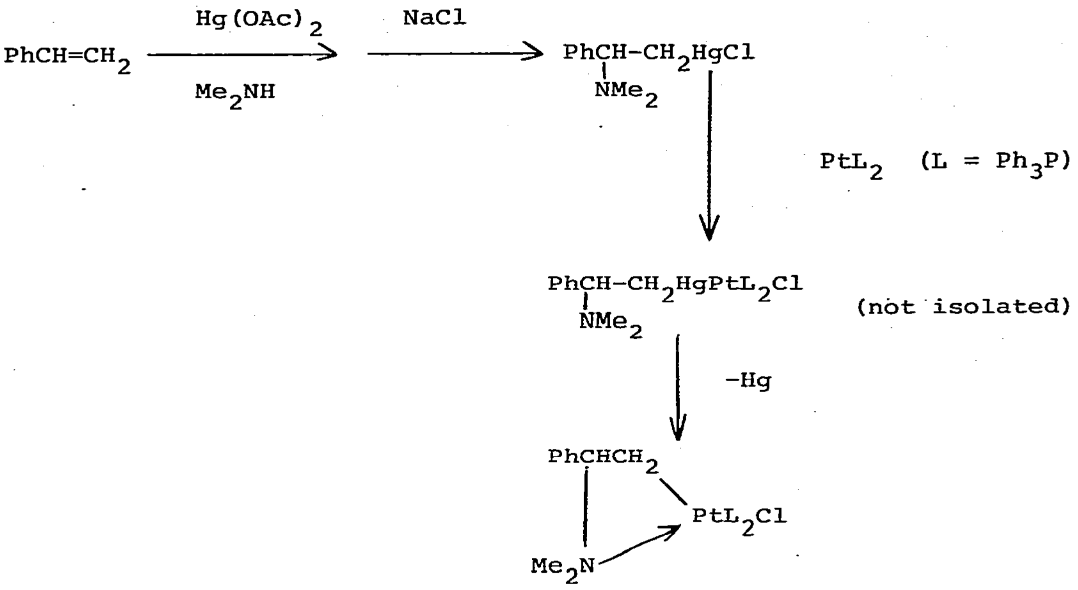
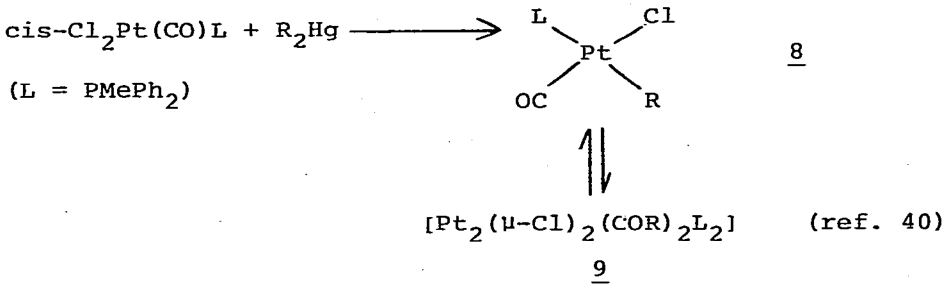
[a] 10 mmol of vinylmercuric chloride, 10 mmol of $PdCl_2$, 20 mmol of LiCl, 100 mmol of alkene, 100 ml of THF, 0°C. [b] Crude yield (recrystallized yield).

product gave a novel chelated Pt(II) complex (39):



Other syntheses include:



Reactions were carried out with Et_2Hg, Ph_2Hg, Me_2Hg and $(PhCH_2)_2Hg$. The equilibrium between the carbonyl complex 8 and the bridged acyl complex 9 depends upon the nature of R: when R = Et, 9 predominates to the extent of 95%; when R = $PhCH_2$, only 8 is present.

$$R_2Hg + [Pr_4N]_2[Cl_4Pt(CO)_2] \xrightarrow[\text{(ref.41)}]{} 2[Pr_4N][RCl_2Pt(CO)] + Hg$$

(R = Me, Et, n-Pr, i-Pr, n-Bu, Ph)

In the reaction above, derivatives with R = t-Bu, $CH_2{=}CH$ and $CH_2{=}CHCH_2$ could not be obtained.

$$\mathrm{Me_2Pt(bipy) + MeHgO_2CCF_3 \longrightarrow Me_3PtO_2CCF_3(bipy)} \qquad \text{(ref.42)}$$

The course of this reaction is complex:

$$\begin{tikzcd}
\mathrm{Me_2Pt(bipy) + MeHgO_2CCF_3} \arrow[r] & \mathrm{Me_2(CF_3CO_2)(HgMe)Pt(bipy)} \arrow[d, "\mathrm{MeHgO_2CCF_3}"] \\
 & \mathrm{Me_2Pt(O_2CCF_3)_2(bipy) + Me_2Hg + Hg} \arrow[d] \\
 & \mathrm{Me_3PtO_2CCF_3(bipy) + MeHgO_2CCF_3}
\end{tikzcd}$$

$PhHgO_2CCF_3$ and $PhHgO_2CCH_3$ react similarly.

The novel and interesting ytterbium derivative $(PhC{\equiv}C)_2Yb$ has been prepared *via* $(PhC{\equiv}C)_2Hg$ (43):

$$\mathrm{(PhC{\equiv}C)_2Hg + Yb \xrightarrow{\text{THF, room temp.}} \underset{(22\%)}{(PhC{\equiv}C)_2Yb} + Hg}$$

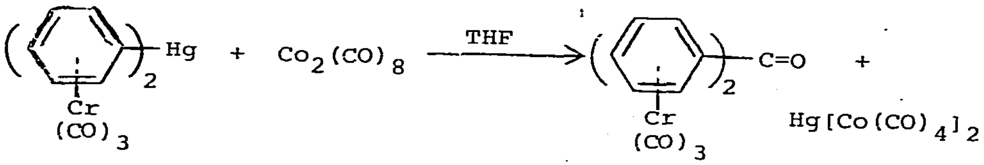
The highly air- and moisture-sensitive product very likely is associated.

B. Application in Organic Synthesis

A review on the use of organomercurials as reagents in organic synthesis has been published (2).

i) Ketones via Organomercurial Acylation and Carbonylation

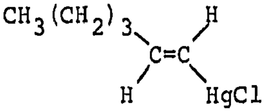
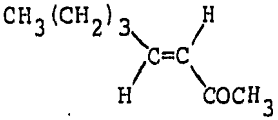
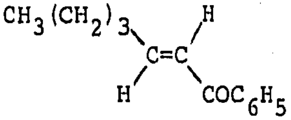
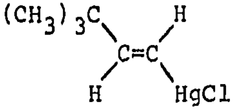
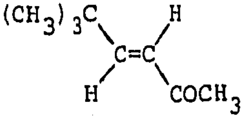
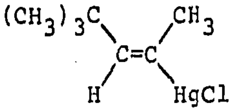
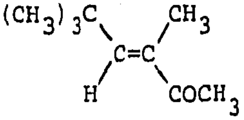
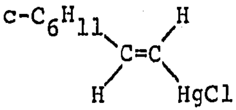
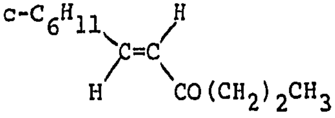
Bis(tricarbonylchromium)-complexed benzophenone has been prepared by the arylmercurial/dicobalt octacarbonyl reaction (44):

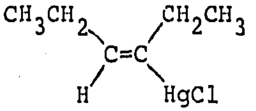
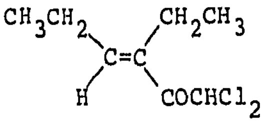
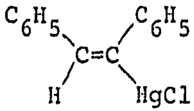
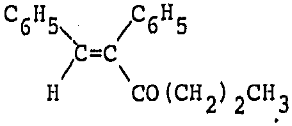
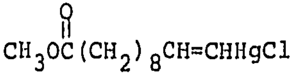
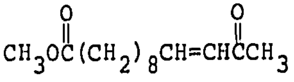
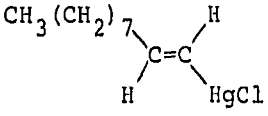
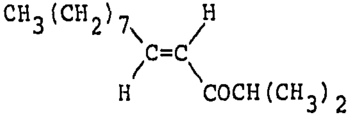
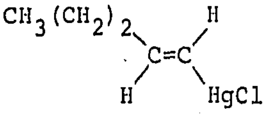
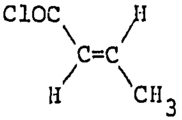
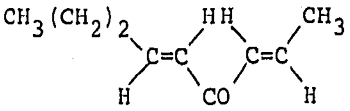
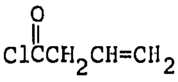
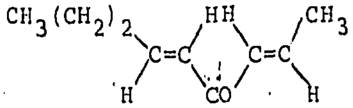


The Lewis acid-induced reaction of acid chlorides with σ-bonded organometallics, which gives ketones, is well known. This general reaction has been applied to the synthesis of α,β-

(Continued on p.162)

TABLE 2. Synthesis of α,β-Unsaturated Ketones via Vinylmercurial/Acid Chloride Reactions (45)^a

Vinylmercurial	Acid Chloride	Ketone	Isolated Yield %
	$ClCOCH_3$		97%
	$ClCOC_6H_5$		64^b
	$ClCOCH_3$		95
			99
	$ClCO(CH_2)_2CH_3$		96

	$ClCOCHCl_2$		89[c]
	$ClCO(CH_2)_2CH_3$		72[d]
 $CH_3OC(=O)(CH_2)_8CH{=}CHHgCl$	$ClCOCH_3$	 $CH_3OC(=O)(CH_2)_8CH{=}CHC(=O)CH_3$	100[e]
	$ClCOCH(CH_3)_2$		97
			97
	 $ClC(=O)CH_2CH{=}CH_2$		91

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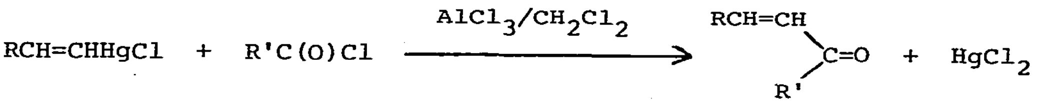
[a] A 10-mmol amount each of vinylmercurial, acid chloride, and aluminum chloride in 100 mL of CH_2Cl_2 stirred for 5 min at room temperature. [b] GLC yield containing 14% cis ketone. [c] Ketone decomposes readily. [d] Ketone separated from a mixture of cis- and trans-stilbene by column chromatography. [e] Both the vinylmercuric chloride and ketone are cis, trans mixtures.

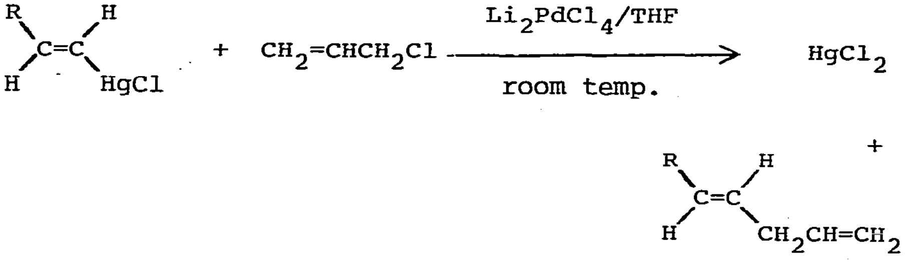
unsaturated ketones from vinylmercurials (45):



The ketones are produced in good yields and high stereochemical purity, and the reaction may be applied to the preparation of functionally substituted enones as well as dienones. What makes this synthesis of practical value is that the vinylic mercurials are readily accessible from acetylenes by way of a hydroboration/ boron-to-mercury transfer sequence. Results are given in Table 2. Reasonable mechanisms for this process include direct electrophilic cleavage of the C-Hg bond by RCO^+ or a two-step sequence involving addition of $RC(O)Cl/AlCl_3$ to the C=C bond of RCH=CHHg-Cl, followed by elimination of $HgCl_2$. The latter was favored by the authors, but the former mechanism was by no means excluded.

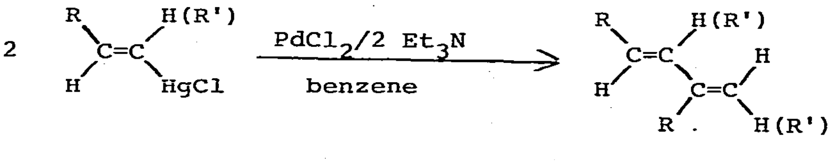
ii) Transition Metal Catalyzed Processes

Vinylmercurials have been used in a palladium chloride-induced reaction with allylic halides to prepare 1,4-dienes (46):

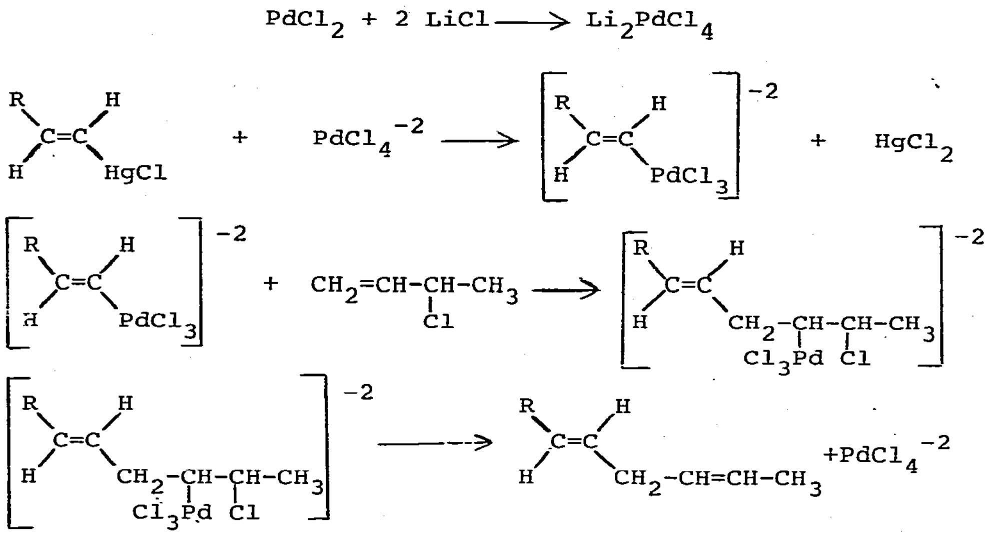


The results are given in Table 3. Some of these reactions proceeded well using only catalytic (10 mole %) amounts of $PdCl_2$, but others required stoichiometric amounts of this reagent. The mechanism shown in Scheme 1, i.e., overall S_N2' substitution of the allylic halide, was suggested.

The reaction of vinylmercurials with palladium chloride/ triethylamine gives head-to-tail coupled 1,3-dienes (47):



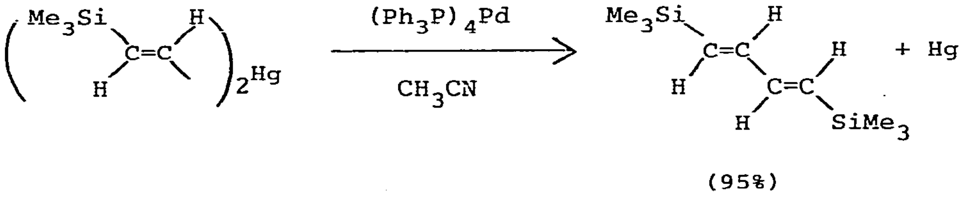
SCHEME 1



Results are presented in Table 4.

A catalytic quantity (10 mole %) of $PdCl_2$ sufficed when two equivalents of anhydrous copper(II) chloride was added to reoxidize the metallic palladium formed in the process. A mechanism involving rearrangement of an intermediate vinylic palladium compound as the key step was suggested.

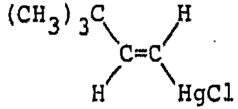
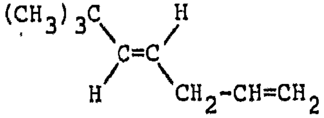
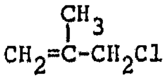
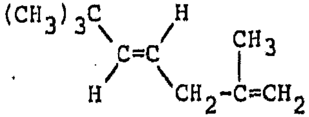
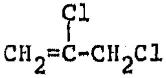
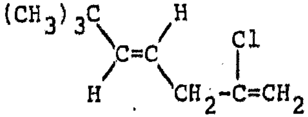
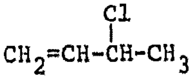
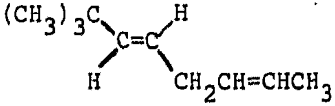
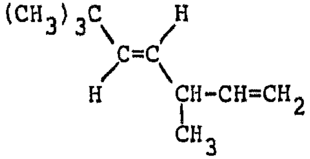
Head-to-head coupling of the vinylic mercurial $(Me_3Si-CH=CH)_2-Hg$ was accomplished using the procedure of Vedejs and Weeks (9):

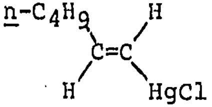
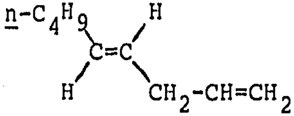
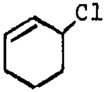
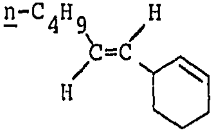
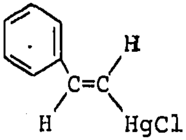
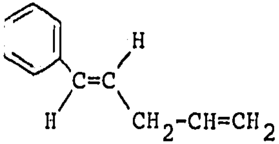
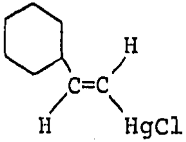
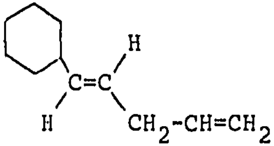
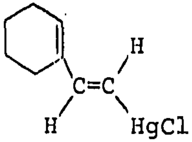
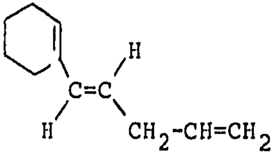


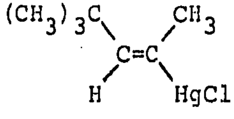
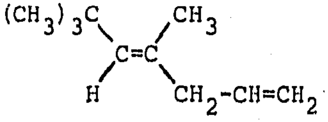
An interesting and useful synthesis of β-chlorobutenolides, which uses the chloromercuration of propargylic alcohols followed by palladium-induced carbonylation of the resulting (E)-β-chloro-γ-

(Continued on p.168)

TABLE 3. Synthesis of 1,4 Dienes from Vinylic Mercurials (46)

Vinylmercurial	Allylic Chloride[a]	1,4-Diene	Yield (%)[b]
	$CH_2=CH-CH_2Cl$		96[c]
	 $CH_2=C(CH_3)-CH_2Cl$		45[d]
	 $CH_2=C(Cl)-CH_2Cl$		28[d]
	 $CH_2=CH-CH(Cl)-CH_3$		49[d]
	$CH_3-CH=CH-CH_2Cl$		32[d]

	$CH_2=CH-CH_2Cl$		71(52)
			39
	$CH_2=CH-CH_2Cl$		80(76)
			73
			100^c

		99 98^{e}

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[a] Ten equivalents and 1 equivalent of palladium chloride unless otherwise indicated.

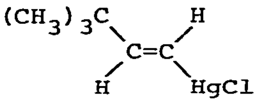
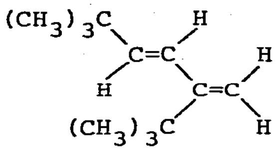
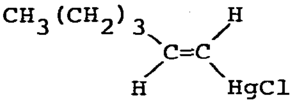
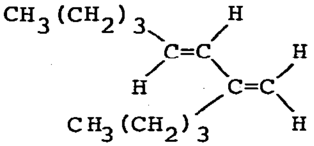
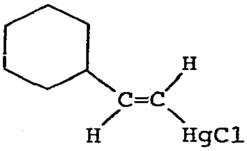
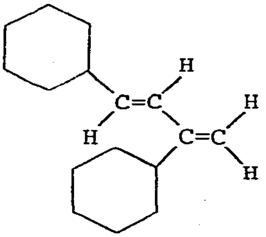
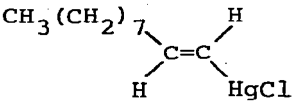
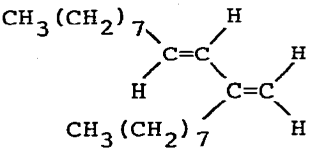
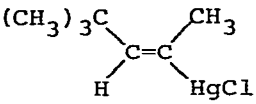
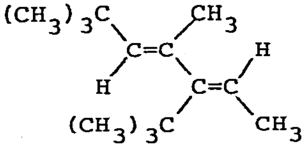
[b] GLC yield (isolated yield).

[c] Five equivalents of allyl chloride and 0.1 equivalent of palladium chloride.

[d] A dimeric product is also seen, probably _trans_, _trans_-2,2,7,7-tetramethyl-3,5-octadiene.

[e] 10% Palladium chloride.

TABLE 4. Synthesis of "Head-to-Tail" Dienes via Vinylmercurials (47)

Vinylmercurial	Diene	Time, h	Yield %[a]
		24	91(6)[b]
		12	98(2) [93](2)
		29	91(2)
		24	[88](5)
		16	62(3) [59](3)

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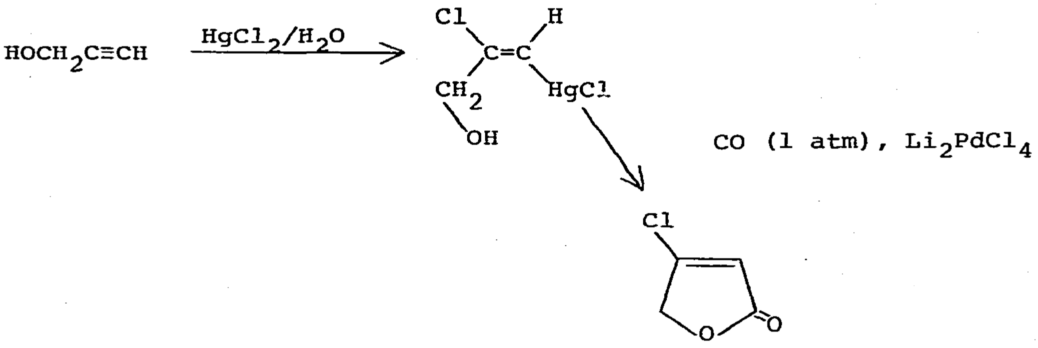
[a] GLC yield using an internal standard; [isolated yield]; (yield of symmetrical 1,3-diene impurity). [b] No triethylamine used.

hydroxyvinylmercuric chloride, has been reported (48):

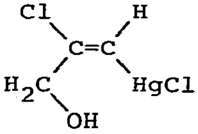
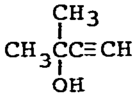
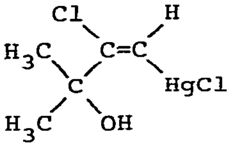


The carbonylation can be effected using either stoichiometric or catalytic amounts of palladium chloride. In the latter case, copper(II) chloride must be used as reoxidant and benzene as the solvent. Table 5 shows the mercuration reactions which were reported. Table 6 brings stoichiometric carbonylation reactions of the mercuration products, Table 7, catalytic carbonylation reactions.

1,3-Dimethyl-2,4-pyrimidinedion-5-ylmercuric acetate, 10, was treated with Pd(OAc)$_2$/LiCl in acetonitrile in the presence of cyclic enol ethers 11, 12 and 13. The 10-derived palladium

(Continued on p.174)

TABLE 5. Chloromercuration of Propargylic Alcohols (48)

Alcohol	Vinylmercurial	% Isolated Yield
HOCH$_2$C≡CH		54
 $CH_3C(CH_3)(OH)C{\equiv}CH$		31

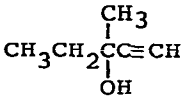
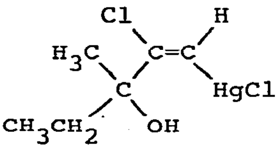
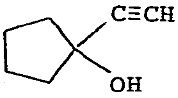
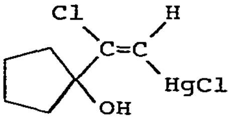
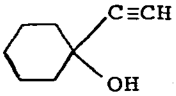
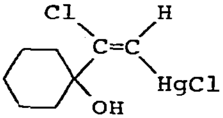
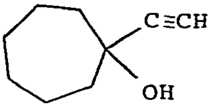
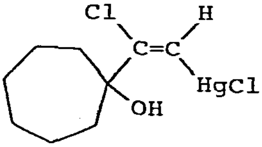
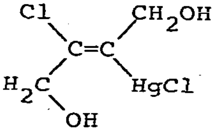
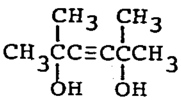
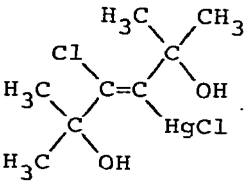
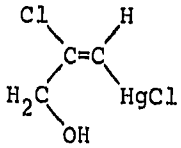
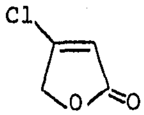
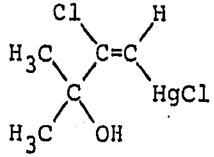
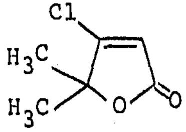
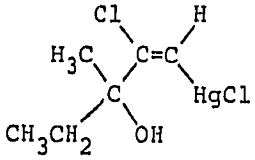
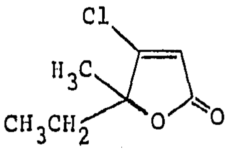
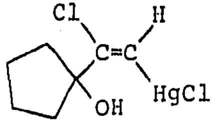
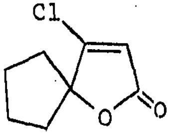
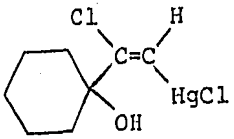
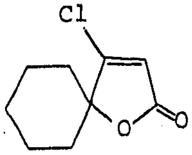
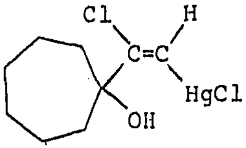
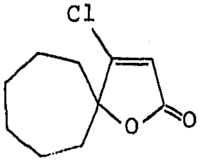
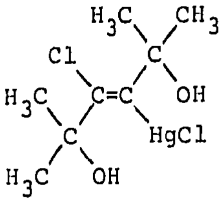
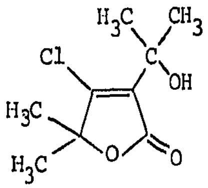
 $CH_3CH_2\overset{CH_3}{\underset{OH}{C}}C\equiv CH$		26
		37
		31
		17
$HOCH_2C\equiv CCH_2OH$		45
 $CH_3\overset{CH_3}{\underset{OH}{C}}C\equiv C\overset{CH_3}{\underset{OH}{C}}CH_3$		85

TABLE 6. Synthesis of Butenolides by Carbonylation of Chloromercuration Products of Propargylic Alcohols. Stoichiometric Reactions (48).[a]

Mercurial	Butenolide	MgO[b]	% Yield
		-	(96)
		- +	92 99(88)
		+	98
		+	99

		- +	58 95(92)
		+	81
		+	94

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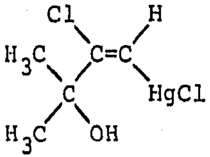
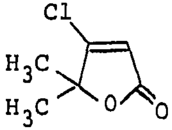
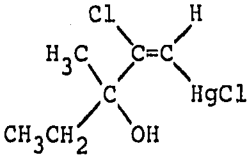
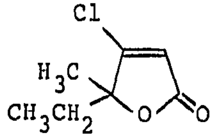
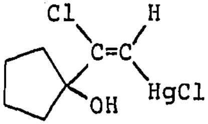
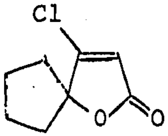
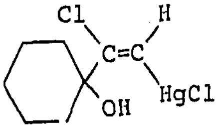
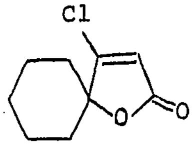
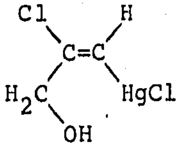
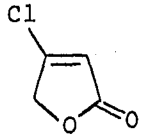
[a] 1 mmol of $PdCl_2$, 2 mmol of LiCl, 10 mL of THF, 5°C, 24 h. [b] 1 mmol or none

TABLE 7. Synthesis of Butenolides by Carbonylation of Chloromercuration Products of Propargylic Alcohols. Catalytic Reactions (48)[a]

Mercurial	% $PdCl_2$ catalyst	Reaction time, h	Butenolide	% Yield
	10 1 1	4 23 46		96 57 99
	10 1	24 120		100 57
	10 1	19 72		93 90

	10 1 1	19 72 432		(81) 54 77
	10 1 1	18 72 40		(78) 45 3

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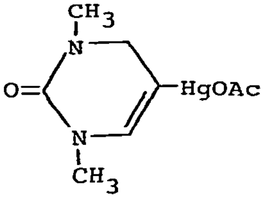
[a] 1 mmol of mercurial, 2 mmol of anhydrous $CuCl_2$, 1 mmol of MgO, 10 mL of benzene at room temperature.



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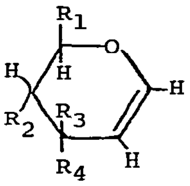
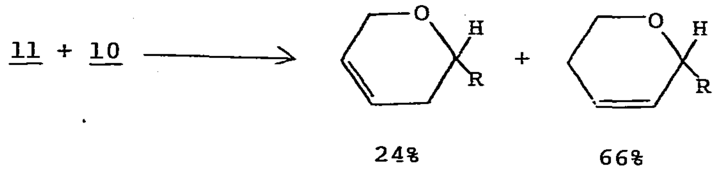


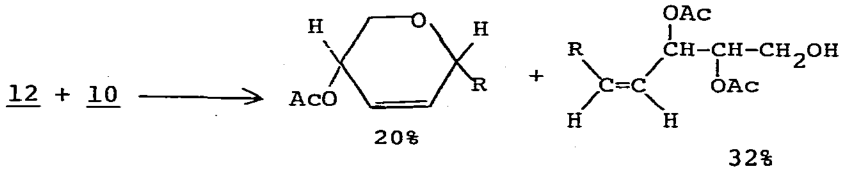
11, $R_1 = R_2 = R_3 = R_4 = H$

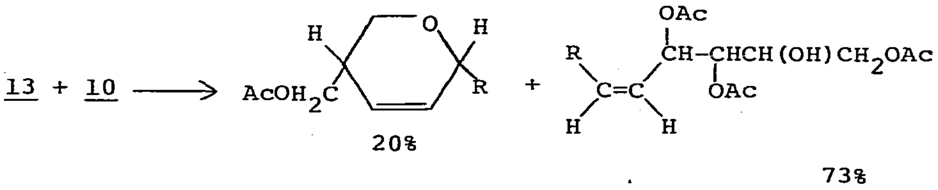
12, $R_1 = R_3 = H$; $R_2 = R_4 = OAc$

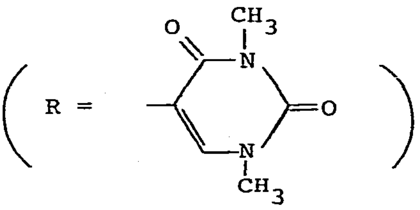
13, $R_1 = CH_2OAc$; $R_2 = R_3 = OAc$;
$R_4 = H$.

intermediate reacted with 11, 12 and 13 to give coupled products (49):



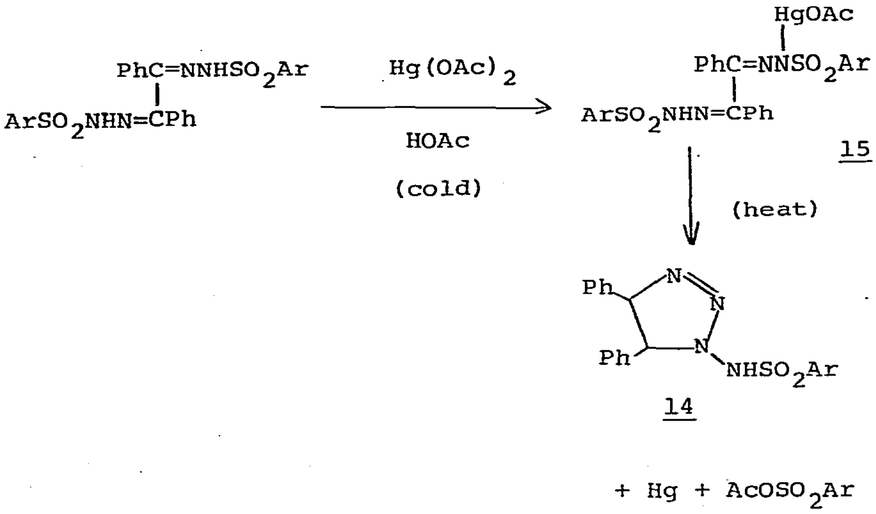


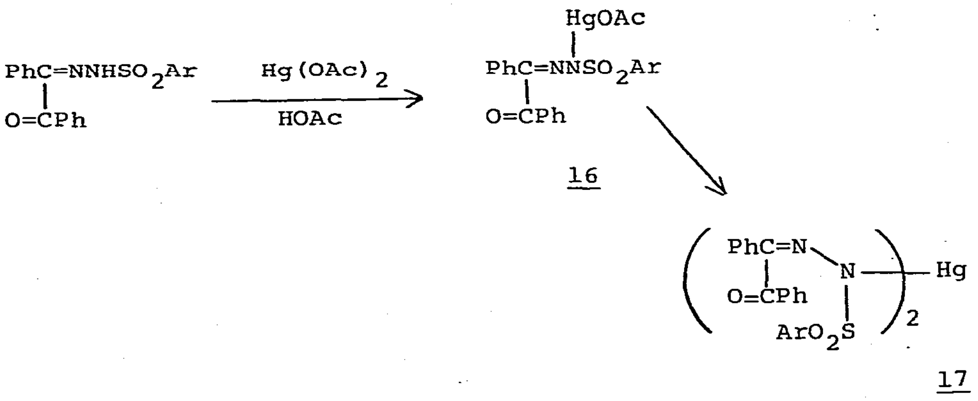




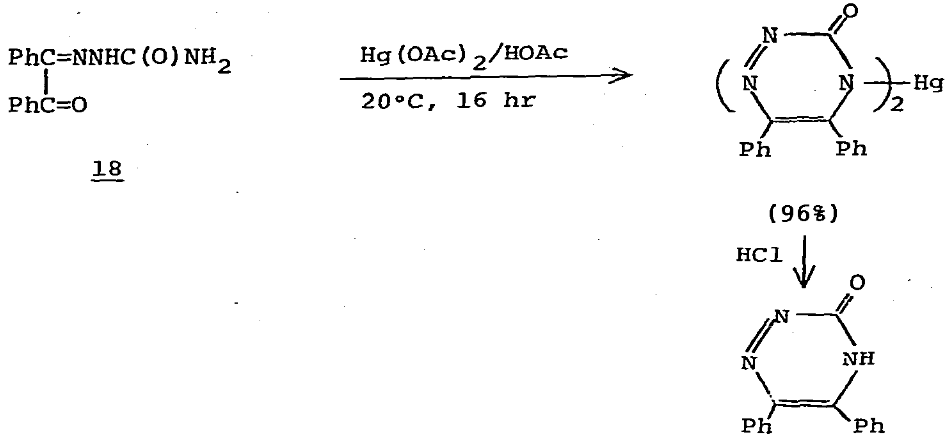
iii) Use of Mercury-Nitrogen and Mercury-Sulfur Derivatives

Mercury-nitrogen and mercury-sulfur derivatives also are useful in organic synthesis. Thus, the oxidation of benzil bis(toluene-p-sulfonyl)hydrazone with $Hg(OAc)_2/HOAc$ gave a cyclic product, 4,5-diphenyl-1,2,3-triazole-1-yl-toluene-p-sulfonamide, 14, via a mercury-nitrogen intermediate (50). The N-mercurated intermediate, 15, could be isolated when the reaction mixture was not heated. In contrast, benzil mono(toluene-p-sulfonyl)-hydrazone, 16, formed a stable mercury product, 17:



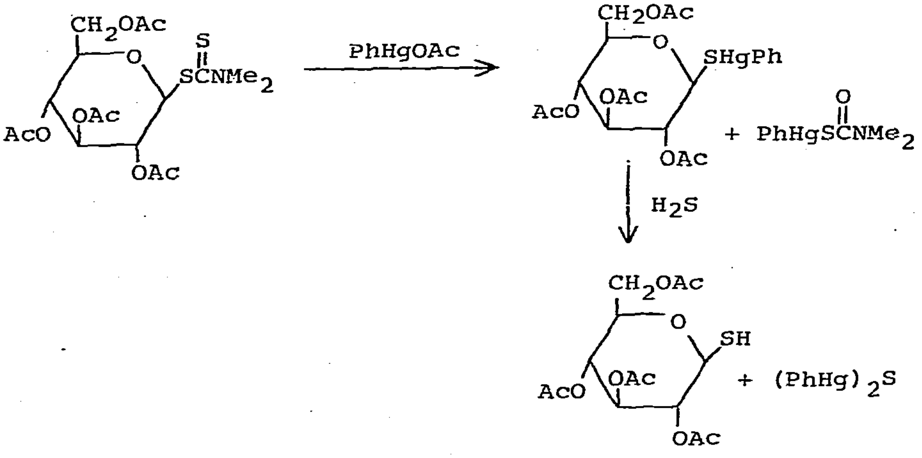


A cyclization also took place when the semicarbazone 18 was treated with mercuric acetate (51):



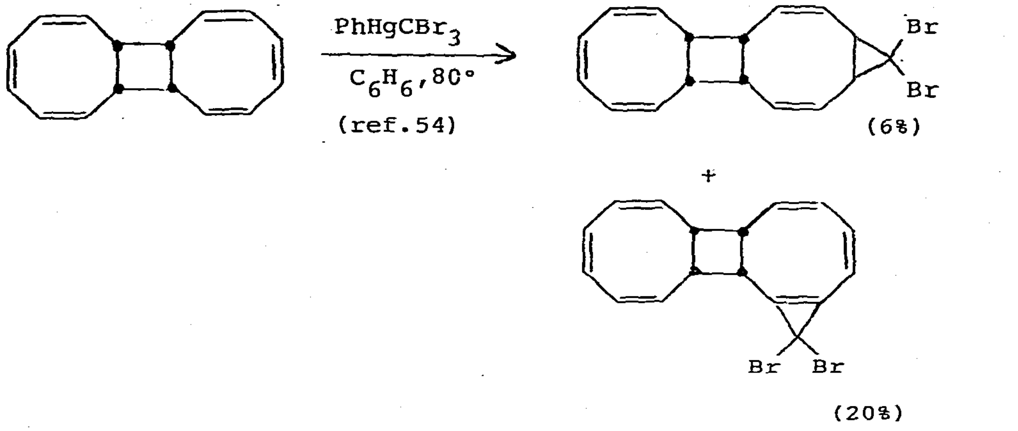
18

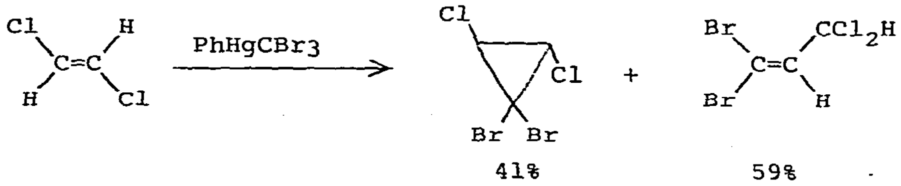
1-Mercurithio-D-glucose derivatives have been used in the synthesis of 1-thio sugars (52):

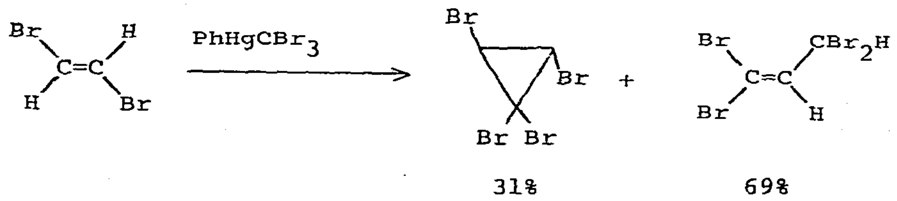


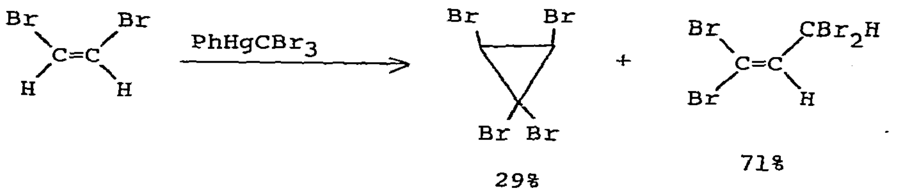
iv) Halomethyl-Mercury Compounds: Divalent Carbon Transfer

The major application of the phenyl(trihalomethyl)-mercurials as dihalocarbene sources in organic chemistry has been in the synthesis of gem-dihalocyclopropanes. During the past year, a rate study of the reactions of $PhHgCCl_3$ and $PhHgCBr_3$ has been reported, in particular, the variation of k_{rel} with temperature of the addition of CCl_2 and CBr_2 derived from these mercurials to $Me_2C=CHMe$ and $Me_2C=CH_2$ (53). New synthetic applications of $PhHgCBr_3$ are given in the equations below.



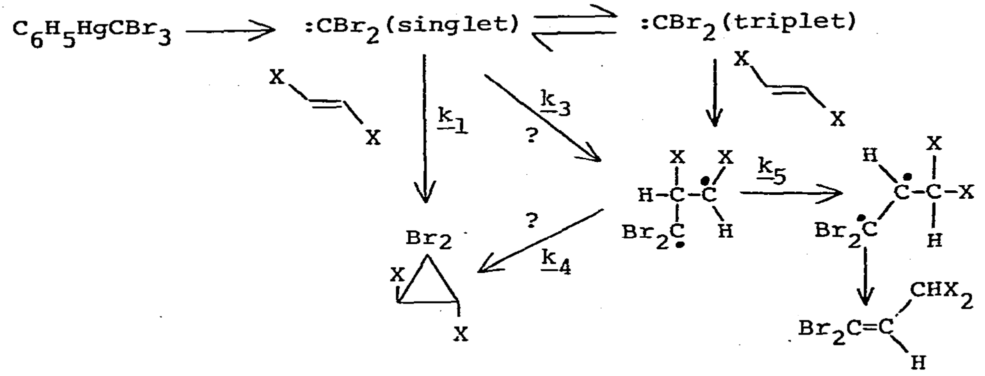




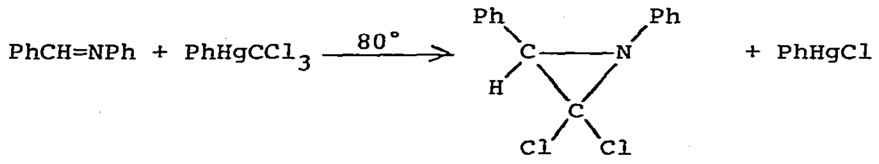


In these experiments with PhHgCBr$_3$/dihaloethylene reactions the olefins are direct reaction products, control experiments having shown that they are not derived from the cyclopropane products in secondary processes. A singlet/triplet equilibrium was suggested to rationalize this result (55) (Scheme 2).

SCHEME 2. Suggested Mechanism of the Reaction of Phenyl(tribromomethyl)mercury with 1,2-Dihaloethylenes (55).

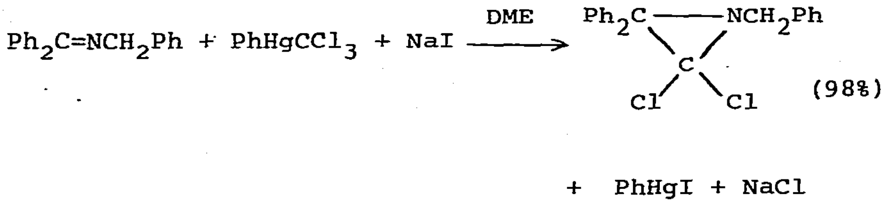


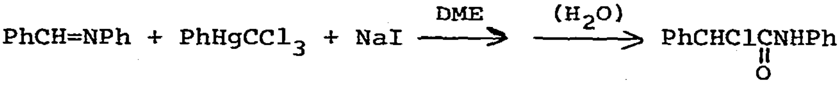
In contrast to a previous report, a *gem*-dichloroaziridine product is obtained in the reactions of $PhHgCCl_2Br$ and $PhHgCCl_3$ with PhCH=NPh (56):



19

However, dichloroaziridine 19 is thermally unstable in the presence of phenylmercuric chloride, undergoing rearrangement to the imidoyl chloride PhCHClC(Cl)=NPh, whose hydrolysis gives PhCHClC(O)NHPh. In a reaction in which a fourfold excess of $PhHgCCl_3$ was used, hydrolytic work-up of this reaction mixture gave this amide in 62% yield. The less stressful sodium iodide procedure gave better results:

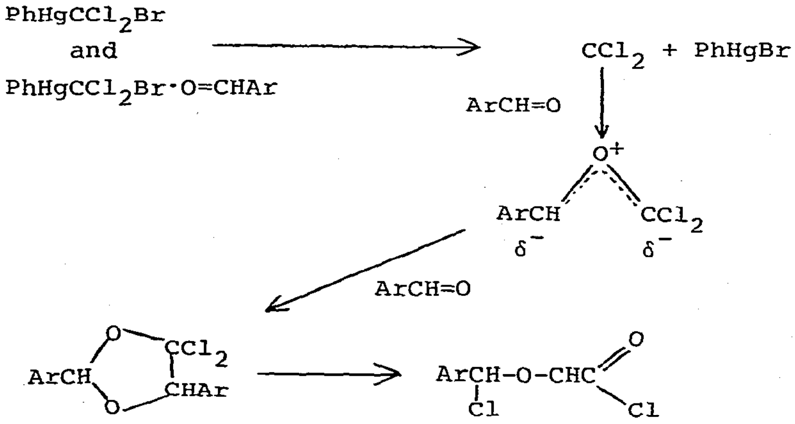




$$PhCH{=}NPh + PhHgCCl_3 + NaI \xrightarrow{DME} \xrightarrow{(H_2O)} PhCHCl\underset{\overset{\|}{O}}{C}NHPh$$

(64%)

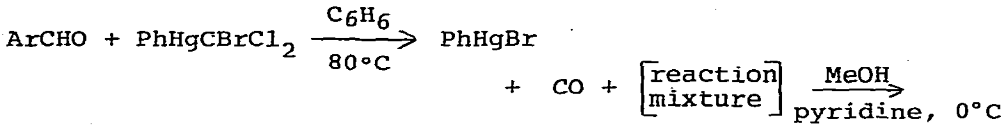
Landgrebe and his coworkers have studied the reactions of $PhHgCCl_2Br$ with substituted benzaldehydes in some detail (57). Table 8 summarizes the major products of reactions carried out in benzene solution at 80°C. Mechanistic studies suggested that CCl_2 is formed initially from the mercurial and a mercurial--aldehyde complex and then is trapped by the aldehyde to form a carbonyl-ylide. Reaction of the latter with a further molecule of aldehyde proceeds <u>via</u> an intermediate dioxolane:



In this study, treatment of the reaction mixture with methanol/ pyridine gave the isolated products, $ArCH(Cl)OCH(Ar)CO_2Me$. A relative reactivity study established the series $Me_2C{=}CMe_2$ cyclohexene > $p\text{-}MeOC_6H_4CHO$ > $n\text{-}C_4H_9CH{=}CH_2$ ∿ PhCHO >> $m\text{-}CF_3C_6H_4\text{-}CHO$ for reactions with $PhHgCCl_2Br$; i.e., the more nucleophilic the carbonyl oxygen, the more reactive is the aldehyde. Of particular interest in this study was IR evidence obtained for the formation of complexes between the phenyl(trihalomethyl) mercurial and benzaldehyde and benzophenone (Table 9).

The insertion of a mercurial-derived halocarbene into a Si-H bond played a key role in the synthesis of tri-tert-butyl-

TABLE 8. Products of $PhHgCCl_2Br$/Substituted Benzaldehyde Reactions (57)



$$ArCHO + PhHgCBrCl_2 \xrightarrow[80°C]{C_6H_6} PhHgBr + CO + \begin{bmatrix}\text{reaction}\\ \text{mixture}\end{bmatrix} \xrightarrow[\text{pyridine, 0°C}]{MeOH}$$

Ar	Additional major products
Ph	$PhCH(OMe)OCHPhCO_2Me$[a] + $PhCHX_2$[b]
3-CF_3Ph	3-$CF_3PhCH(OMe)OCH(3$-$CF_3Ph)CO_2Me$[c] + 3-$CF_3PhCHCl_2$
4-MeOPh	4-$MeOPhCHX_2$ + 4-$MeOPhCH(OMe)_2$ + 4-$MeOPhCHOHCO_2Me$
2,4,6-Me_3Ph	2,4,6-Me_3PhCHX_2

[a] Diasteriomer ratio, 1.8:1. [b] Known to be a substantial mixture of benzal chloride and α-chloro-α-bromotoluene. [c] Diastereomer ratio, 1.2:1.

TABLE 9. Benzaldehyde and Benzophenone Complexes with $PhHgCCl_2Br$ (57)

Compd	$\tilde{\nu}CO$[a] (free)	$\tilde{\nu}CO$ com- (plexed)	$\Delta\tilde{\nu}CO$	K_{eq}[b]	K_{eq}'[c]
PhCHO	1708.0	1696.0	12	0.57±0.07	4.5±0.5
Ph_2CO	1663.5	1647.5	16	0.56±0.01	2.8±0.1

[a] $\tilde{\nu}$ are given in cm^{-1} and were measured in degassed benzene under argon at ca. 25°C. [b] For an assumed 1:1 complex. [c] For an assumed 1:2 (mercurial-ligand complex.

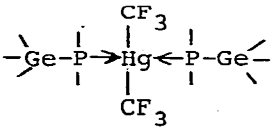
methylsilane (58):

$$\begin{tikzcd}(Me_3C)_3SiH + PhHgCHBr_2 \arrow[r, "C_6H_5Cl,\ reflux"] & (Me_3C)_3SiCH_2Br + PhHgBr \arrow[d, "n\text{-}Bu_3SnH"] \\ & (Me_3C)_3SiCH_3\end{tikzcd}$$

A remarkable new type of CF_2 insertion reaction has been reported by Escudié, Couret and Satgé (59), e.g.:

$$Me_3GePMe_2 \xrightarrow{Hg(CF_3)_2} Me_3GeCF_2PMe_2 \quad (30\%)$$

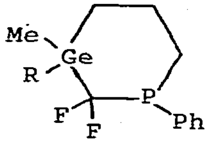
Germylphosphines form 2:1 complexes, 20, with bis(trifluoromethyl)-mercury in benzene. On being heated to 80°C, the adducts 20 decompose as follows:



20

$$2\ Me_3GePMe_2 \cdot Hg(CF_3)_2 \longrightarrow (Me_2P)_2Hg + 2\ Me_3GeF + 2\ CF_2$$

Under the reaction conditions, the bisphosphinomercury compound decomposes to metallic mercury and $Me_2P\cdot$ radicals; the latter are intercepted by CF_2. They also can dimerize to tetramethyl-diphosphine which reacts with $(CF_3)_2Hg$ by a radical displacement process to give Me_2PCF_3. Difluorocarbene insertion into the Ge-P bond of Me_3GePMe_2 gives $Me_3GeCF_2PMe_2$. A similar reaction of bis(trifluoromethyl)mercury with 2,2-dimethyl-2-germa-1-phenyl-1-phospholane gave 21 (R = Me). The insertion process



21

is stereospecific, according to experiments with a 70/30 diastereoisomeric mixture of 21 (R = Ph), but it is not known whether a retention or an inversion process is involved. The former was reasonably assumed and a three-center transition state was suggested.

4. MERCURATION OF UNSATURATED COMPOUNDS

A. Olefins

While the reaction of mercury(II) salts with olefins usually results in formation of β-functional ethylmercurials ("solvomercuration"), the action of mercury(II) salts on 1,1-diarylethylenes gives vinylic mercurials. This reaction has been studied in some detail by Sokolov, Bashilov and Reutov (60). These reactions are observed with the more ionic HgX_2 salts with weakly nucleophilic X substituents (CF_3CO_2, NO_3, BF_4):

$$Ar_2C{=}CH_2 + HgX_2 \longrightarrow Ar_2C{=}CHHgX \xrightarrow{Cl^-(Br^-)} Ar_2C{=}CHHgCl(Br)$$

Dimercurated products, $Ar_2C{=}C(HgX)_2$, also can be obtained in such reactions. Table 10 gives the reported results. A terminal $=CH_2$ group is required; $Ph_2C{=}CHR$ (R = Me, Ph, Br) give no vinylic mercurials. In the presence of suitable nucleophiles, solvomercuration products also are obtained. The mechanism is outlined in Scheme 3.

Scheme 3. Mechanism of $Ar_2C{=}CH_2/HgX_2$ Reactions (60).

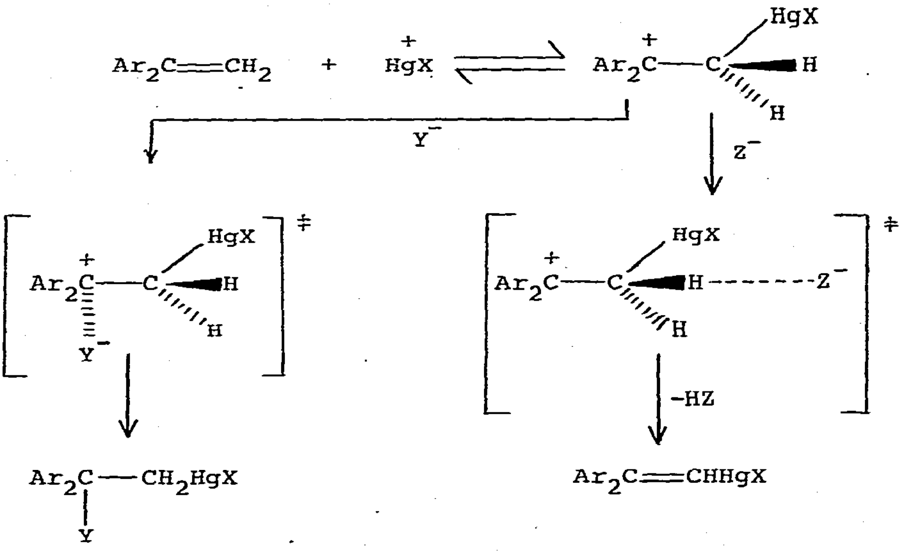
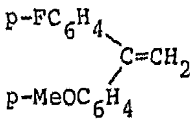
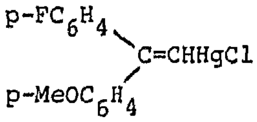
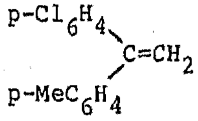
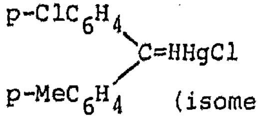
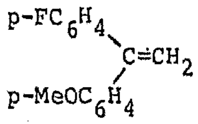
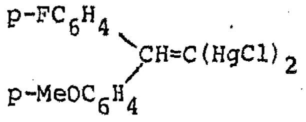
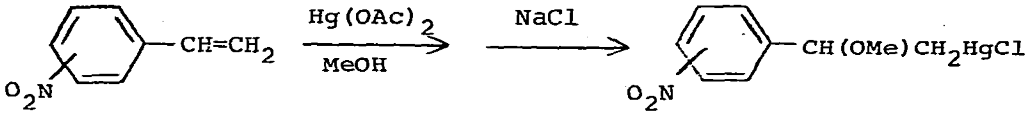


TABLE 10. Reactions of 1,1-Diarylethylenes with Mercury(II) Salts (60).

Olefin	X in HgX_2	Solvent	Product, after Cl^- or Br^--for-X^- Exchange (%Yield)
$Ph_2C=CH_2$	CF_3CO_2	benzene	$Ph_2C=CHHgBr$ (85)
$Ph_2C=CH_2$	NO_3	acetonitrile	$Ph_2C=CHHgCl$ (78)
$(p\text{-}MeC_6H_4)_2C=CH_2$	CF_3CO_2	benzene	$(p\text{-}MeC_6H_4)_2C=CHHgBr$ (74)
$(p\text{-}MeC_6H_4)_2C=CH_2$	CF_3CO_2	benzene	$(p\text{-}MeC_6H_4)_2C=CHHgBr$ (91)
$(p\text{-}ClC_6H_4)_2C=CH_2$	CF_3CO_2 (+ $BF_3\cdot OMe_2$)	diethyl ether	$(p\text{-}ClC_6H_4)_2C=CHHgCl$ (95)
$(p\text{-}MeOC_6H_4)_2C=CH_2$	CF_3CO_2 (+ $BF_3\cdot OMe_2$)	diethyl ether	$(p\text{-}MeOC_6H_4)_2C=CHHgCl$ (90)
 $\begin{matrix}p\text{-}FC_6H_4\\ p\text{-}MeOC_6H_4\end{matrix}\rangle C=CH_2$	NO_3	acetonitrile	 $\begin{matrix}p\text{-}FC_6H_4\\ p\text{-}MeOC_6H_4\end{matrix}\rangle C=CHHgCl$ (80) (isomer mixture)
 $\begin{matrix}p\text{-}Cl_6H_4\\ p\text{-}MeC_6H_4\end{matrix}\rangle C=CH_2$	NO_3	acetonitrile	 $\begin{matrix}p\text{-}ClC_6H_4\\ p\text{-}MeC_6H_4\end{matrix}\rangle C=HHgCl$ (61) (isomer mixture)
 $\begin{matrix}p\text{-}FC_6H_4\\ p\text{-}MeOC_6H_4\end{matrix}\rangle C=CH_2$	NO_3	acetonitrile	 $\begin{matrix}p\text{-}FC_6H_4\\ p\text{-}MeOC_6H_4\end{matrix}\rangle CH=C(HgCl)_2$ (16)
$(p\text{-}MeC_6H_4)_2C=CH_2$	NO_3	acetonitrile	$(p\text{-}MeC_6H_4)_2C=C(HgCl)_2$ (54)

The oxymercuration of o- and p-nitrostyrene was studied by Russian workers (61):



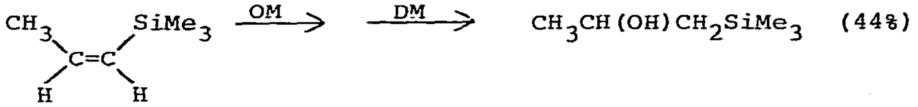
The oxymercuration-demercuration of vinylic and allylic silanes has been investigated (62):

$$Me_3SiCH{=}CH_2 \xrightarrow{Hg(OAc)_2/aq.\ THF^*} \xrightarrow{NaBH_4/aq.NaOH^{**}} MeSiCH_2CH_2OH\ (90\%)$$

$$(\underline{no}\ Me_3SiCH(OH)CH_3)$$

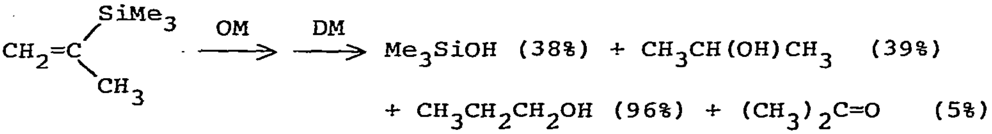
(This result confirms a previous study; Seyferth and Kahlen, 1959)

$$CH_2{=}CHCH_2CH_2SiMe_3 \xrightarrow{OM} \xrightarrow{DM} CH_3CH(OH)CH_2CH_2SiMe_3 \quad (99\%)$$



$$\overset{CH_3}{\underset{H}{C}}{=}\overset{SiMe_3}{\underset{H}{C}} \xrightarrow{OM} \xrightarrow{DM} CH_3CH(OH)CH_2SiMe_3 \quad (44\%)$$

By-products in the last reaction were Me_3SiOH (25%), $CH_3CH(OH)$-CH_3 (19%) and $CH_3CH_2CH_2OH$ (7%). A complication appears to be Si-C cleavage by the Hg(II) species to give cis-propenylmercuric acetate whose oxymercuration produces $CH_3CH(OH)CH(HgOAc)_2$. Reduction of the latter gives 2-propanol.



$$CH_2{=}C\begin{matrix}SiMe_3\\CH_3\end{matrix} \xrightarrow{OM} \xrightarrow{DM} Me_3SiOH\ (38\%) + CH_3CH(OH)CH_3\ (39\%)$$
$$+\ CH_3CH_2CH_2OH\ (96\%) + (CH_3)_2C{=}O \quad (5\%)$$

Elemental mercury and mercury(I) acetate were formed during the course of the oxymercuration of isopropenyltrimethylsilane.

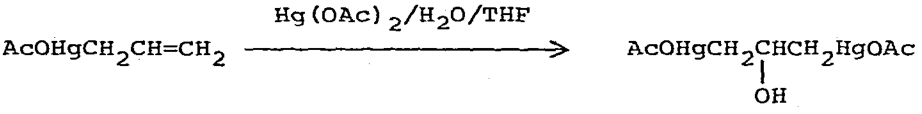
---

[*] $Hg(OAc)_2/aq.THF$ = oxymercuration = OM in subsequent equations.

[**] $NaBH_4/aq.\ NaOH$ = demercuration = DM in subsequent equations.

$$Me_3SiCH_2CH{=}CH_2 \xrightarrow{OM} \xrightarrow{DM} Me_3SiOH\ (44\%) + (Me_3Si)_2O\ (7\%) + CH_3CH(OH)CH_3\ (25\%) + CH_3CH_2CH_2OH\ (10\%)$$

In the latter reaction the initial process which occurs appears to be C-Hg bond cleavage to give allylmercuric acetate. The latter then is oxymercurated:

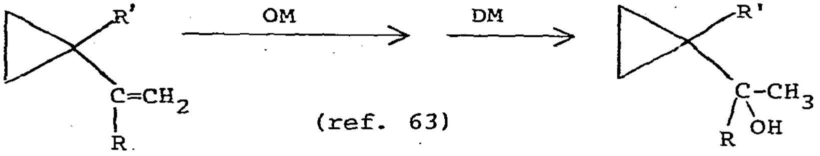


$$AcOHgCH_2CH{=}CH_2 \xrightarrow{Hg(OAc)_2/H_2O/THF} AcOHgCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2HgOAc$$

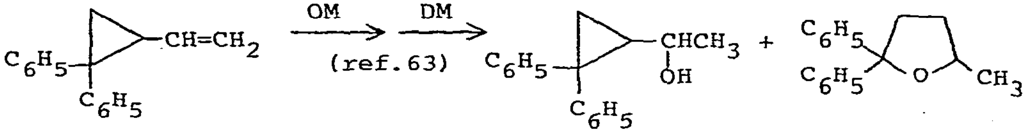
22

Sodium borohydride demercuration of the dimercurial 22 which is formed results in the formation of $CH_3CH(OH)CH_3$.

Other examples of olefin oxymercuration or of the oxymercuration/demercuration sequence have been reported.

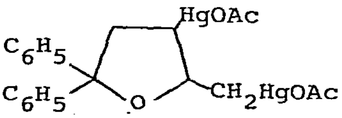


(R = cyclo-C_3H_5, R' = H;
R = Ph, R' = H;
R = H, R' = Me)



(83%) 23 (17%)

Reduction with $NaBD_4$ served to show that the tetrahydrofuran derivative 23 has bis-mercurial 24 as its immediate precursor. The



24

following scheme was proposed:

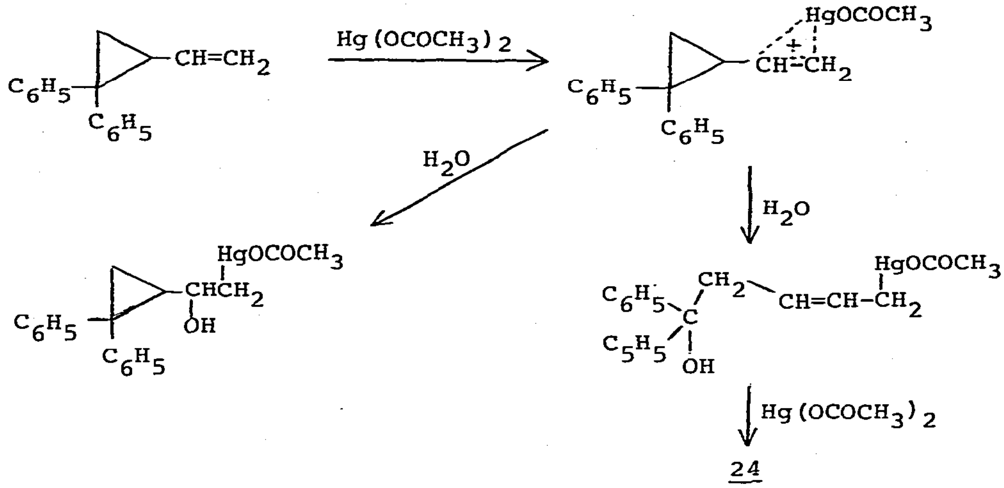
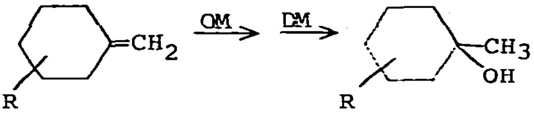


TABLE 11. Oxymercuration/demercuration of Substituted Methylenecyclohexanes and -cyclopentanes (64)

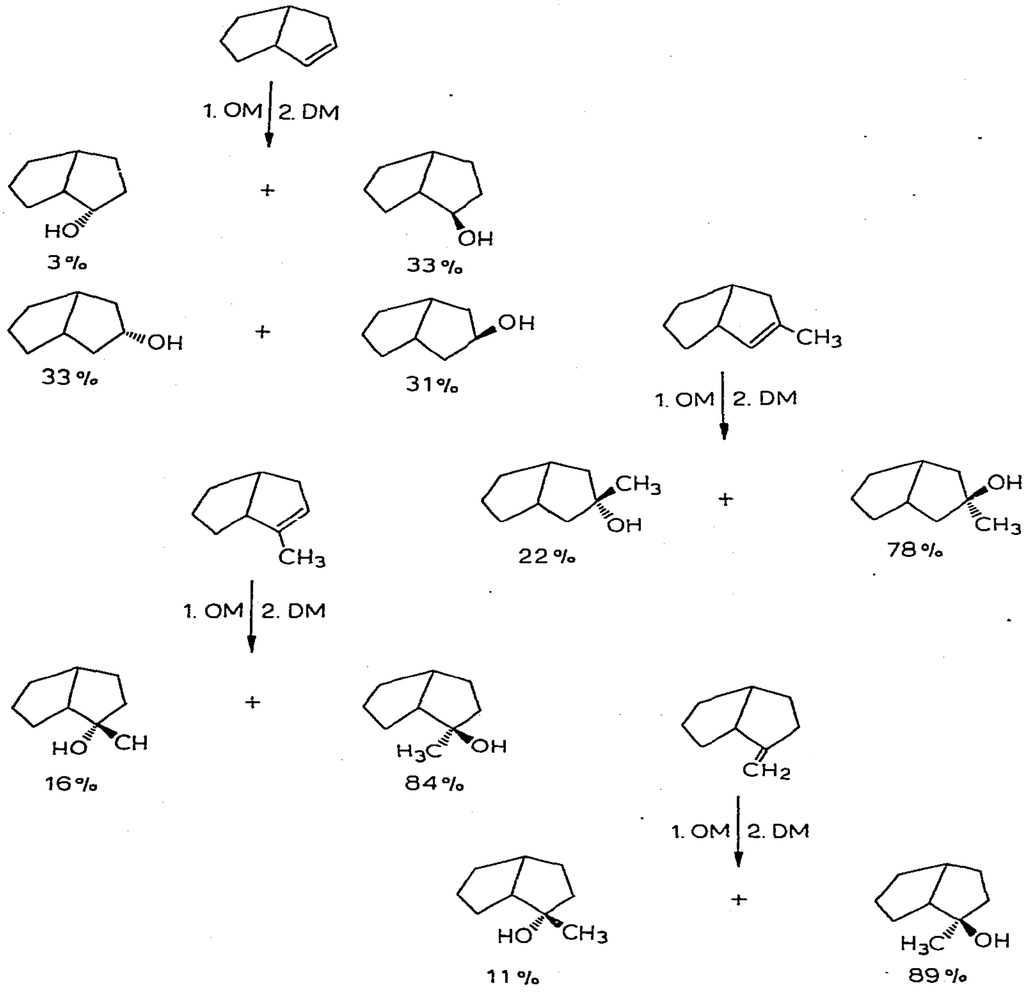
	Reaction conditions	
Methylenecyclohexanes	0°C, 15 min Product %	20°C, 15 min (axial attack)
2-Methyl-	33	37
2-Isopropyl-	30	34
2-t-Butyl	3	4
3-Methyl	54	54
3-t-Butyl	58	58
4-Methyl-	68	69
4-t-Butyl	71	69
cis-2-Methyl-4-t-butyl	44	
trans-2-Methyl-4-t-butyl	79	
2,2-Dimethyl-4-t-butyl	73	71
3,3,5-Trimethyl-	71	70
trans-2-Isopropyl-5-methyl-	24	25
Methylenecyclopentanes	Product % (cis attack)	
2-Methyl-	90	79
2-Cyclopentyl-	72	71
2-t-Butyl	No reaction	

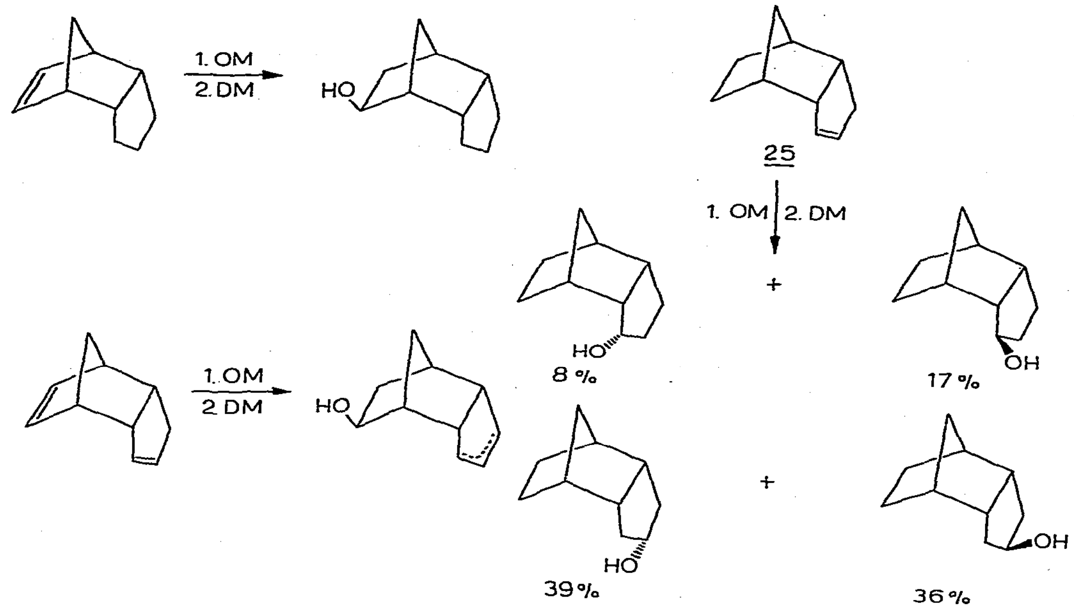
Substituted methylenecyclohexanes have been oxymercurated/demercurated to give substituted cyclohexanols (64):



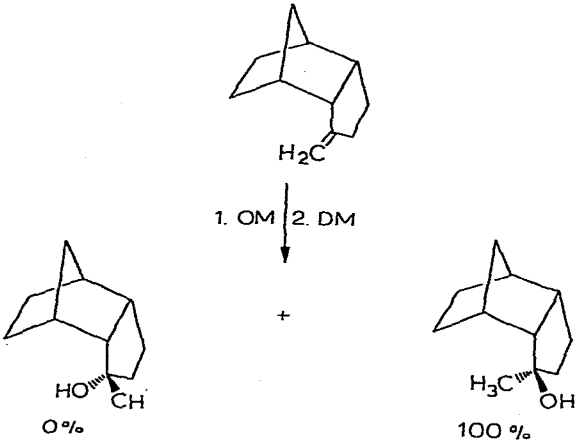
Of interest in this study was the product stereochemistry. With unhindered methylenecyclohexanes the attack of OH^- on the ionic intermediate occurs on the axial side; this situation changes when bulky substituents are present, as Table 11 shows.

Brown and Hammar have investigated the stereochemistry of the OM/DM of cis-bicyclo[3.3.0]oct-2-ene, endo-trimethylenenorbornene and related olefins (65):

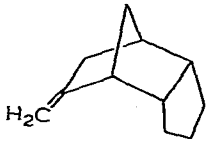




(The reaction of olefin 25 with $Hg(OAc)_2$ in aqueous THF was very slow and the products very likely are those of thermodynamic, not kinetic, control. A faster reaction, but not a significantly different product distribution, was observed with $Hg(O_2CCF_3)_2$.)

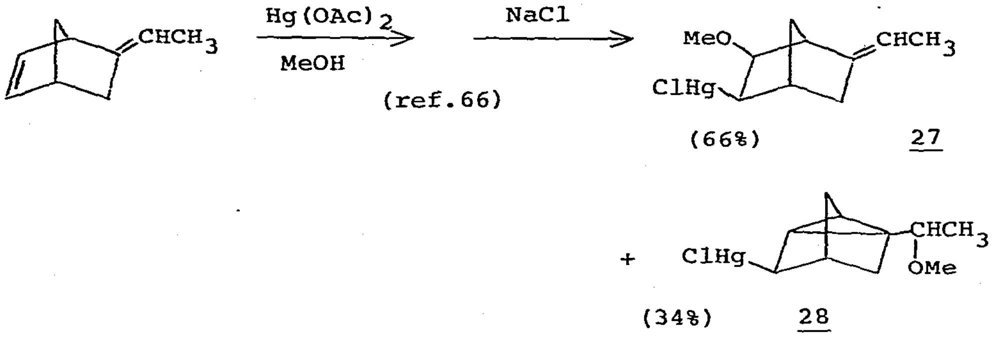


Olefin 26 failed to undergo oxymercuration under the standard reaction conditions which were successful with the other olefins studied.



26

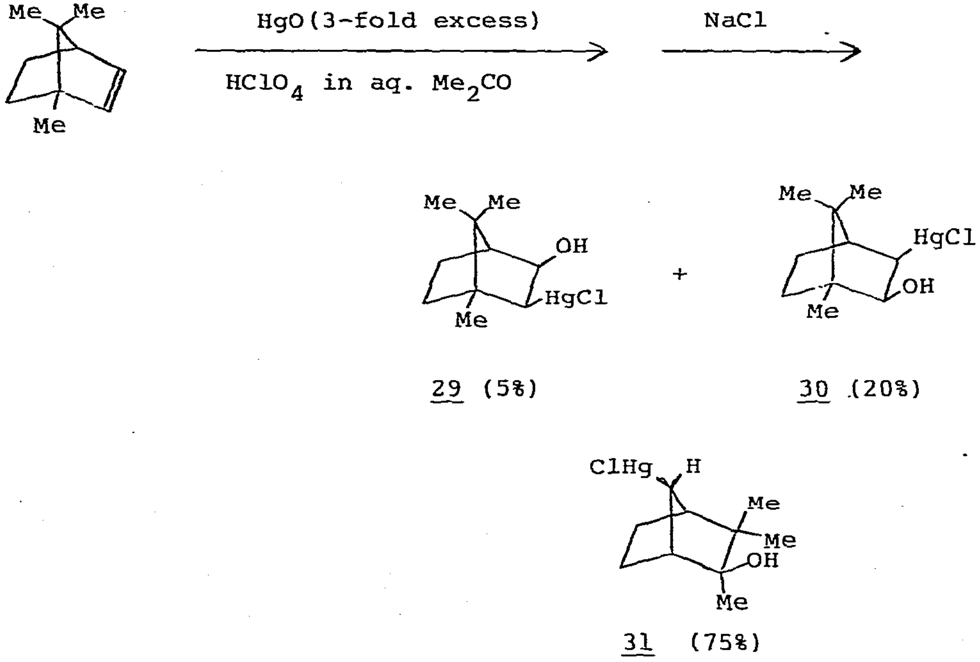
Other workers have studied the oxymercuration of bicyclic olefins:



(66%) 27

(34%) 28

The ratio of the yields of 27 and 28 is solvent-dependent. Solvents of high dielectric constant (water, aq. THF, methanol) lead to formation of the 1,5-addition product 28 (91% yield of 28 in water solution), but in glacial acetic acid or anhydrous THF only 27 is produced.

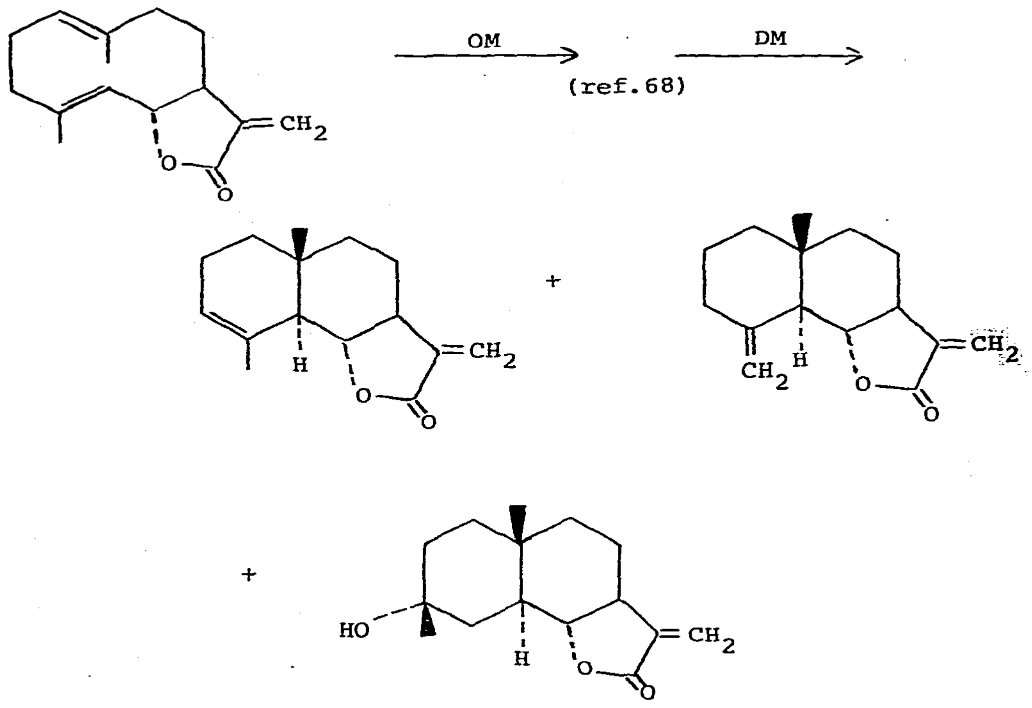


29 (5%)

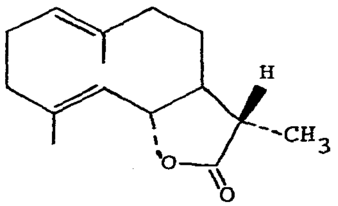
30 (20%)

31 (75%)

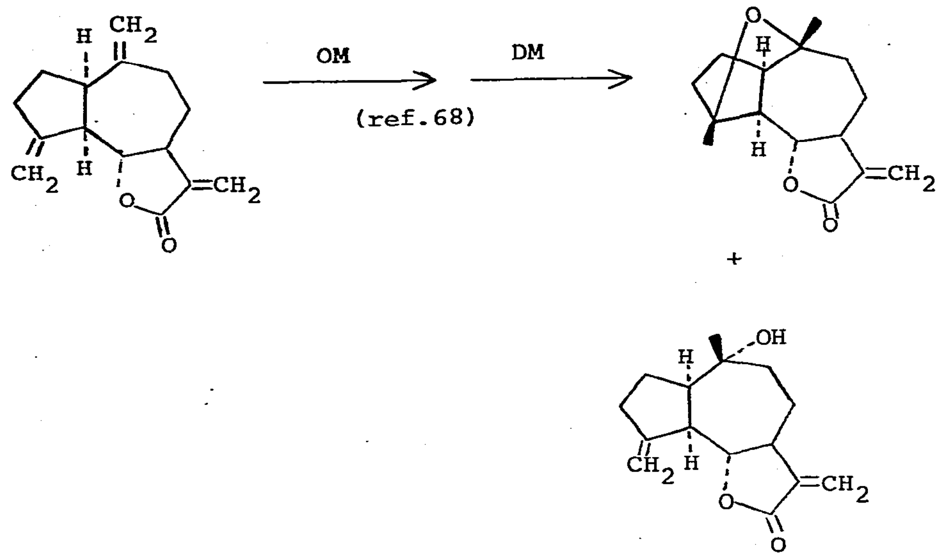
In the reaction above, the rearrangement product 31 is not formed by isomerization of 29 and 30, rather it is a directly formed reaction product. Its yield decreases as the $HClO_4/HgO$ ratio is decreased (67).



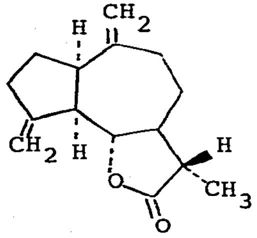
Products analogous to those in the equation above were obtained in the oxymercuration/demercuration of 32.



32

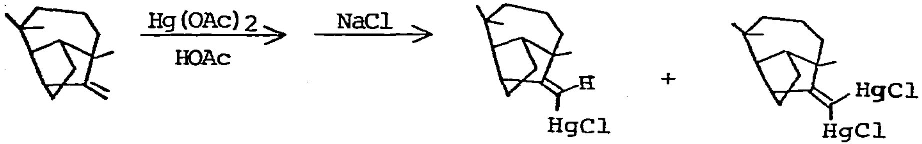


Analogous products were obtained with 33.



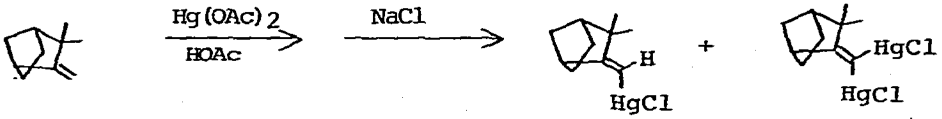
33

In the above experiments with methylenelactone derivatives the exo-methylene substituent of the α-methylene-γ-lactone was unreactive toward mercuric acetate.



34 35 36

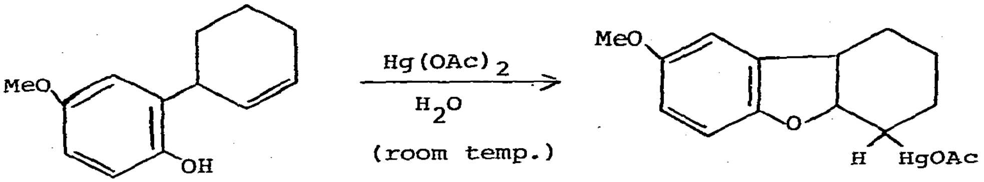
As shown above, mercuration of longifolene, 34, gave 35 and 36 (69). Halogen cleavage of these products resulted in formation of the respective mono- and di-bromides and mono- and di-iodides Camphene reacted similarly:



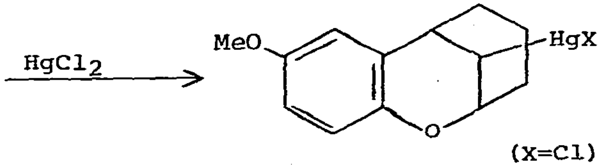
37

In both cases, mercuration of the mono-mercurated products in separate experiments gave the dimercurials, 36 and 37, respectively.

In the examples below, the electronic effect of the substituent on mercury (X in HgX_2) is important in determining the regioselectivity (70):

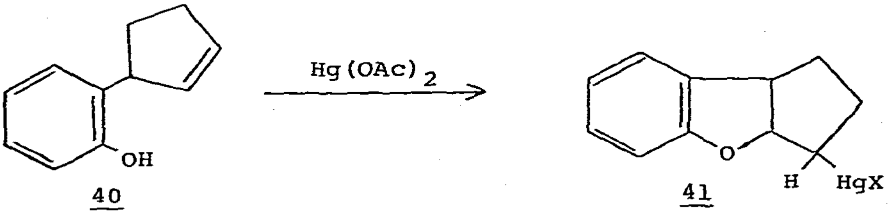


38



39

Reaction of 38 with $Hg(NO_3)_2$, $Hg(ClO_4)_2$, $Hg(O_2CCl_3)_2$ and $Hg(O_2CCF_3)_2$ gave the chroman 39 (X = NO_3, ClO_4, O_2CCl_3 and O_2CCF_3, respectively); $Hg(O_2CCH_2Cl)_2$ and $Hg(O_2CCHCl_2)_2$ gave mixtures of both types of products.



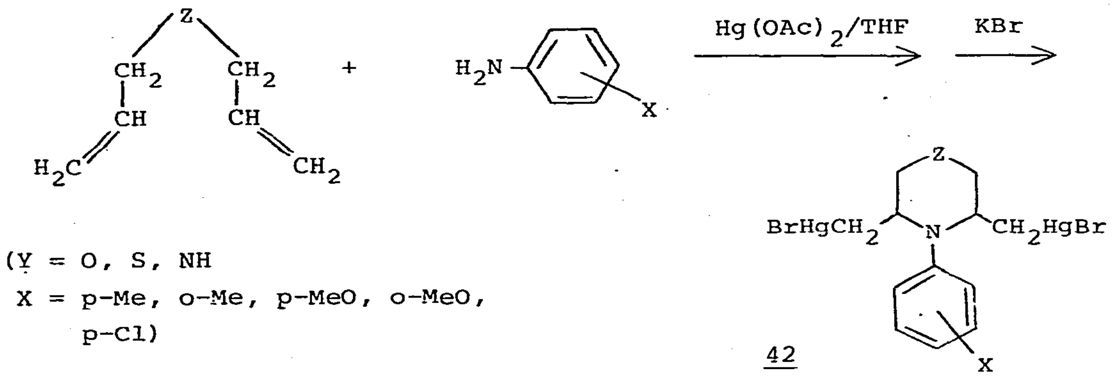
40

41

(X = OAc)

Reaction of 40 with mercuric chloride gave 41 (X = Cl). In this case the chroman isomeric with 41 is too strained for its formation to be favorable.

The aminomercuration of diallyl ether, diallyl sulfide and diallyl amine provides a facile route to mercurated morpholines, tetrahydro-1,4-thiazines and hexahydropyrazines (71):



(Y = O, S, NH
X = p-Me, o-Me, p-MeO, o-MeO,
p-Cl)

42

Sodium borohydride reduction of 42 (Z = O) in alkaline medium gave demercurated morpholines. In the case of the compound where Y = S and NH, C-N bond fission occurred:

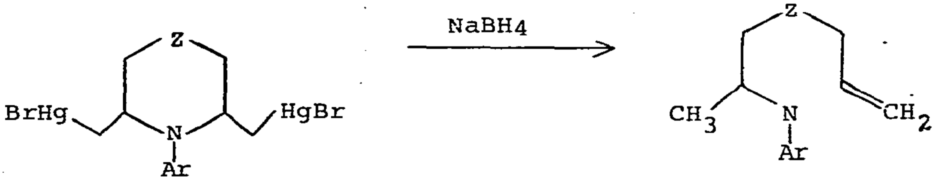
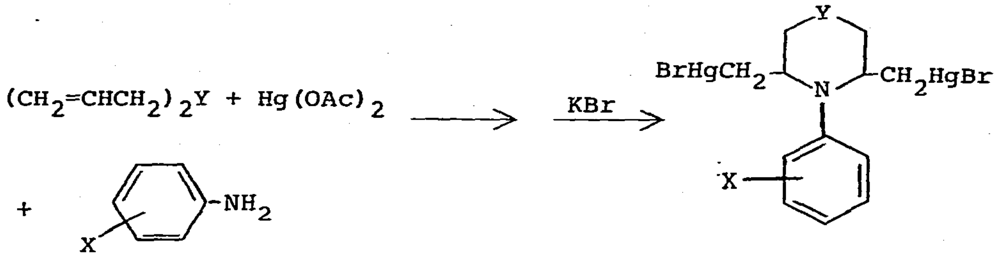


Table 12 gives details of the preparation of 42.

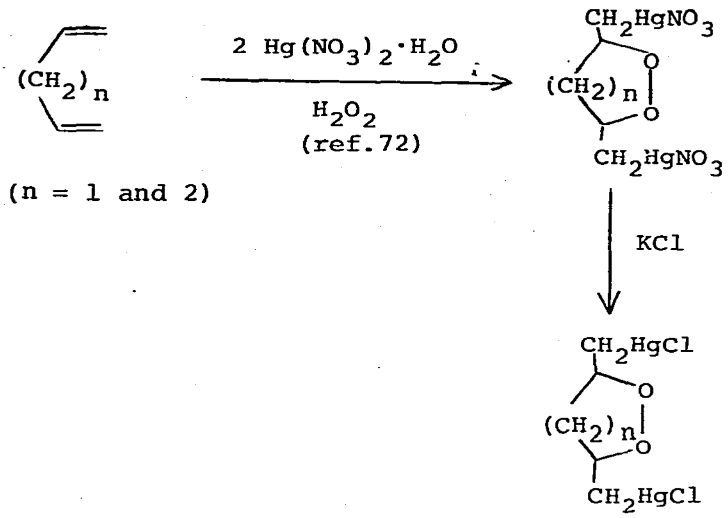
Several papers have dealt with the preparation of cyclic peroxides by the peroxymercuration of dienes.

TABLE 12. Preparation of Mercurated Heterocyclic Compounds from Diallyl Ether, Diallyl Sulfide and Diallylamine (71)



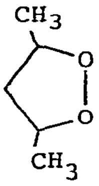
Y	X	Reaction Conditions		Yield[a]
		$Ar\text{-}NH_2/Hg^{2+}$	Time	[%]
O	H	8/1	5 min	100
S	H	8/1	3 h	100
NH	H	5/1	5 min	100
O	4-CH_3	4/1	3 h	100
S	4-CH_3	4/1	22 h	85
NH	4-CH_3	3/1	40 min	99
O	4-OCH_3	2/1	7 h	81
S	4-OCH_3	3/1	25 h	83
NH	4-OCH_3	3/1	1 h	100
O	4-NO_2	2.5/1	2 d	80
S	4-NO_2	3/1	4 d	62
NH	4-NO_2	3/1	20 h	68
O	4-Cl	3/1	30 min	96
S	4-Cl	3/1	3 h	98
NH	4-Cl	2/1	30 min	96
O	2-CH_3	4/1	5 h	100
O	2-OCH_3	4/1	3 h	87

[a] Based on diene 1.

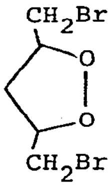


43

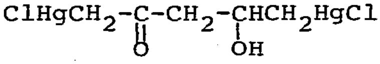
Reactions of 43 (n = 1) with alkaline $NaBH_4$, bromine and pyridine produced 44, 45 and 46, respectively.



44

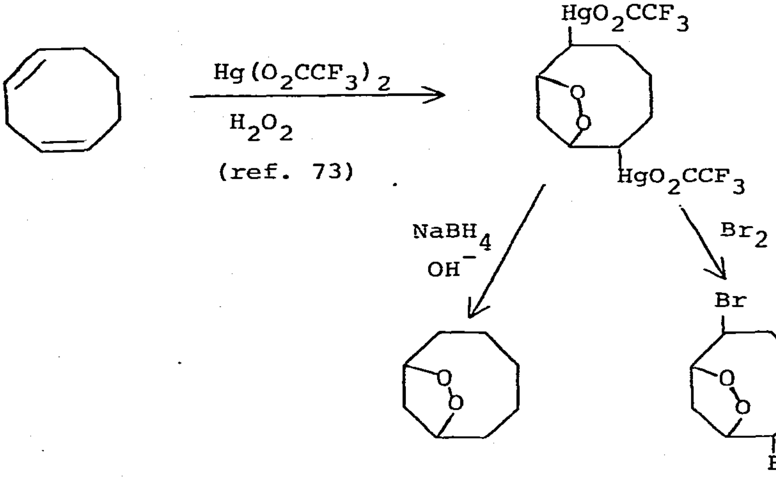


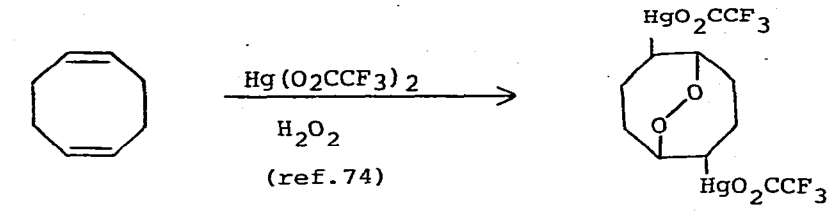
45

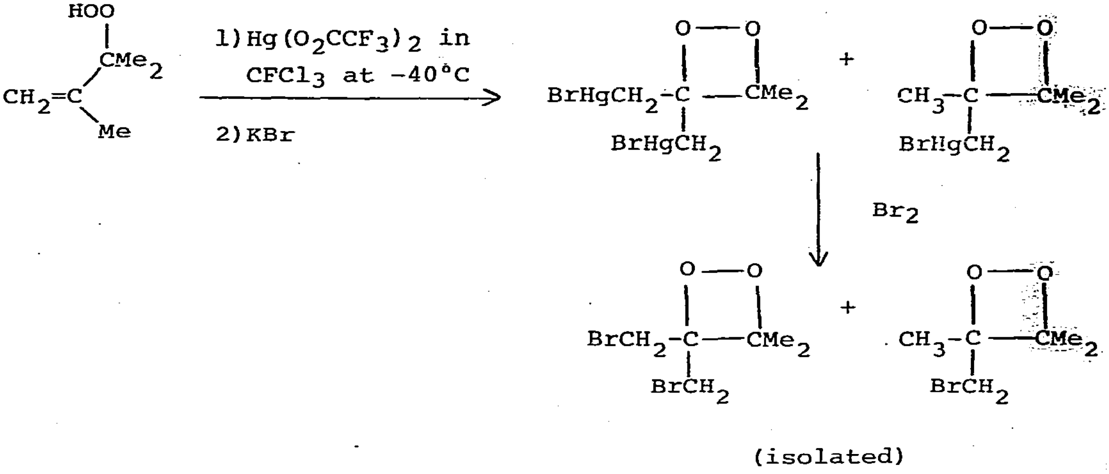


$\mathrm{ClHgCH_2-\underset{\overset{\|}{O}}{C}-CH_2-\underset{\overset{|}{OH}}{C}HCH_2HgCl}$

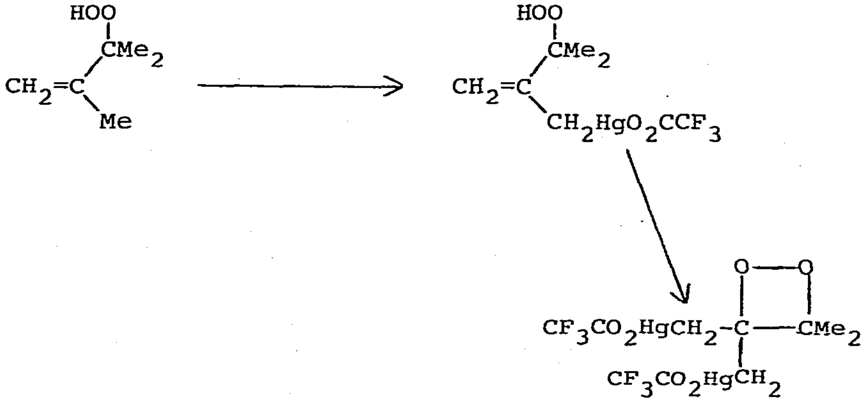
46



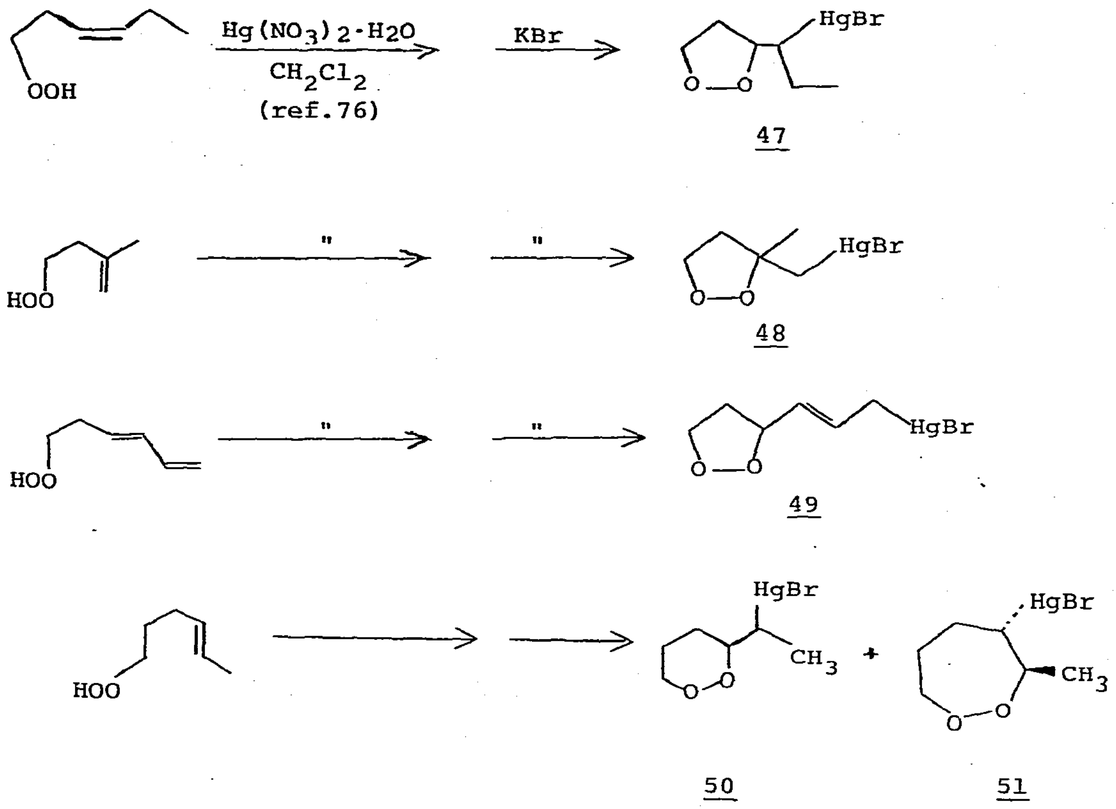




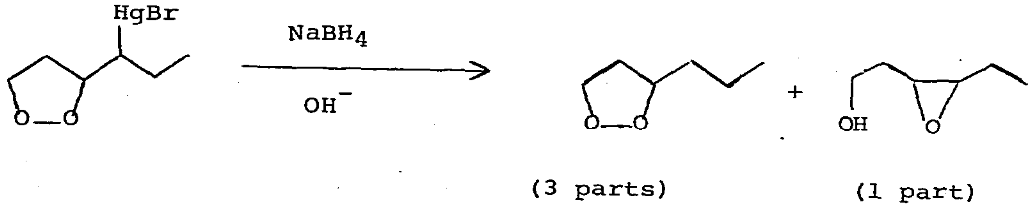
The dimercurated product was formed <u>via</u> an initial allylic mercuration product:



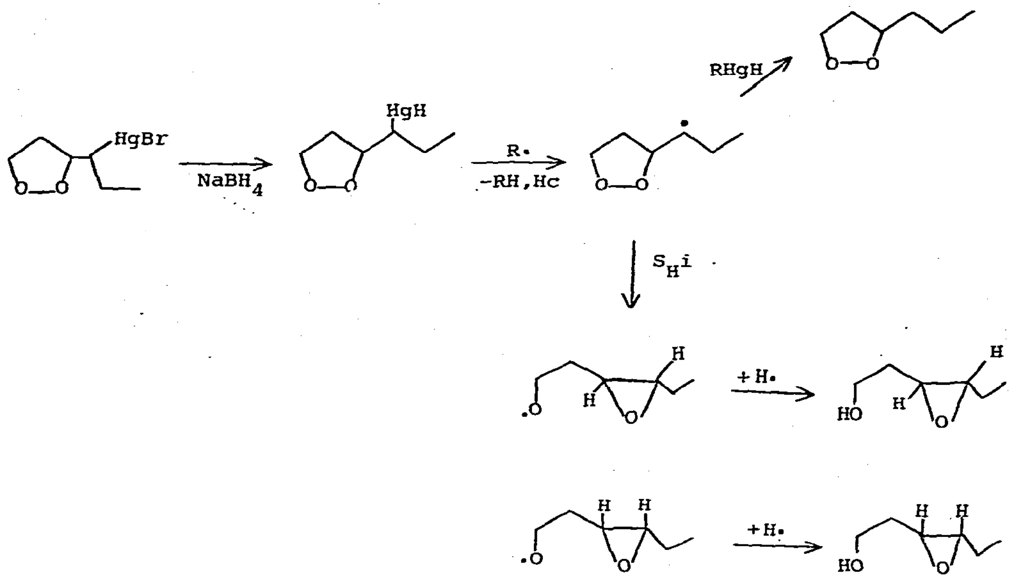
The mercurated dioxetanes could not be isolated, but their brominolysis and their $LiAlH_4$ reduction products were characterized (75).



These cyclic peroxy-mercurials were demercurated with basic NaBH$_4$ and bromodemercurated in dichloromethane and in pyridine medium. Demercuration of <u>47</u>, <u>48</u>, <u>50</u> and <u>51</u> was accompanied by formation of epoxy alcohols, e.g.:

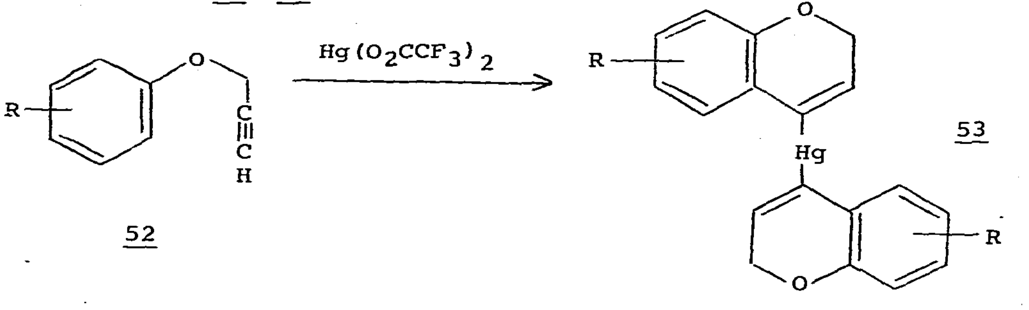


The mechanism below was suggested for this reaction (76):



B. Acetylenes

The reaction of mercury(II) trifluoroacetate with aryl 2-propynyl ethers, 52, followed by treatment of the reaction mixture with alkaline sodium borohydride (demercuration conditions) gave organomercury products, 4,4'-bis(2H-chromenyl)-mercurials, 53 (77):



52

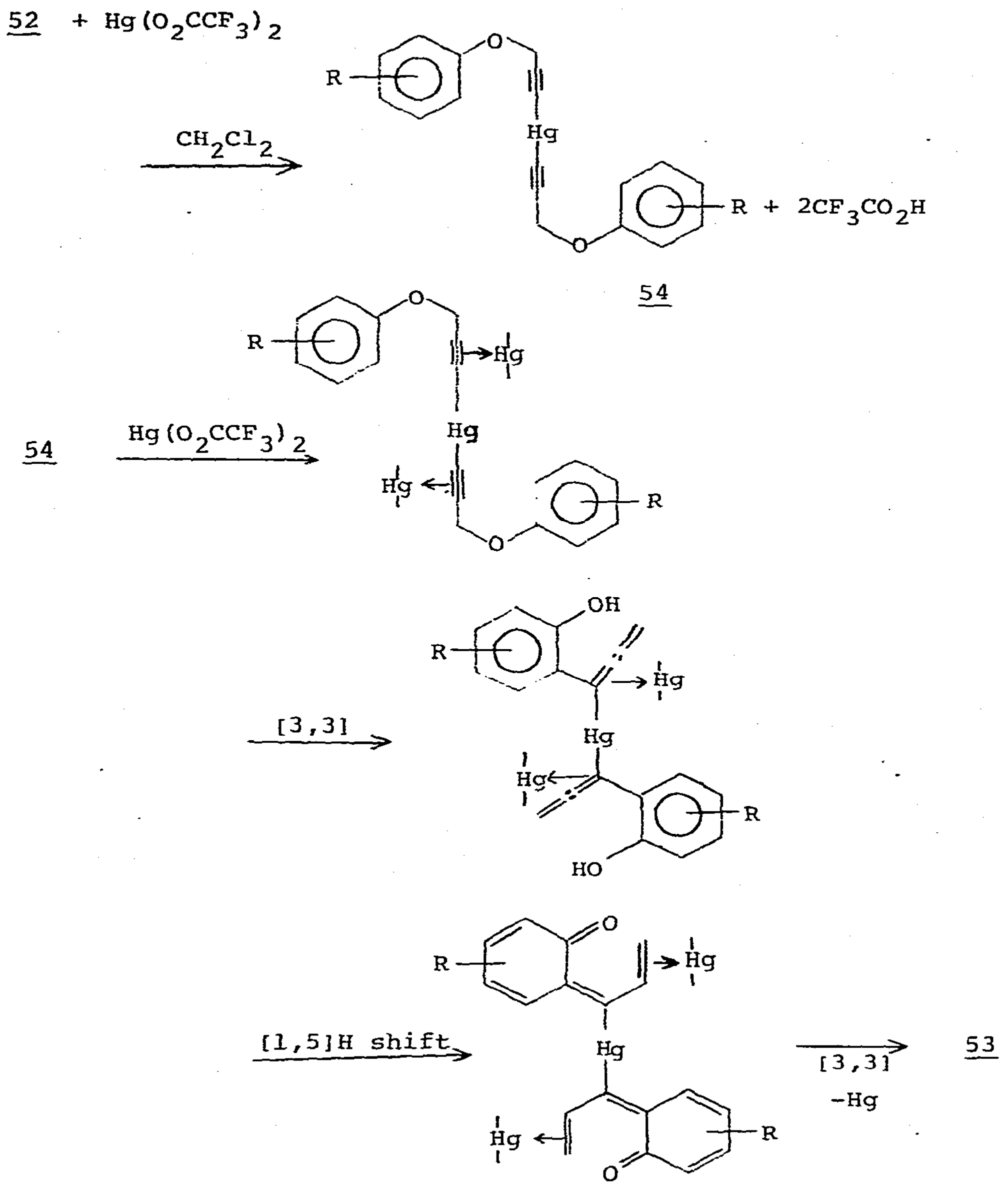
53

$+ 2\ CF_3CO_2H$

The formation of 53 was rationalized in terms of Scheme 4.

When bis-alkynylmercurials of type 54 (prepared by known routes) were subjected to the reaction conditions which served to convert the aryl 2-propynyl ethers to 53, products of this type

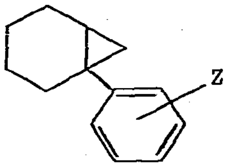
SCHEME 4



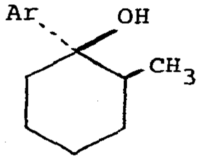
also were obtained, thus supporting the idea of their intermediacy.

C. Cyclopropanes

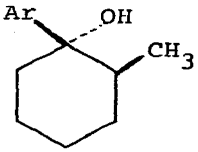
The stereochemistry of the nucleophilic step in the ring opening reactions of 1-arylbicyclo[4.1.0]heptanes, 55, with mercuric salts has been investigated (78). The results suggested that intermediates with a high degree of carbocationic character are involved. The cis/trans ratio of the product obtained after demercuration of the mercurials formed in the cyclopropane ring opening reaction, 56/57, varied markedly with change in the Hg(II) salt used ($Hg(OAc)_2$, $Hg(O_2CCF_3)_2$, $Hg(NO_3)_2$, $Hg(ClO_4)_2$) and the reaction conditions.



55 a = H
b = $p-CH_3$
c = m-Cl

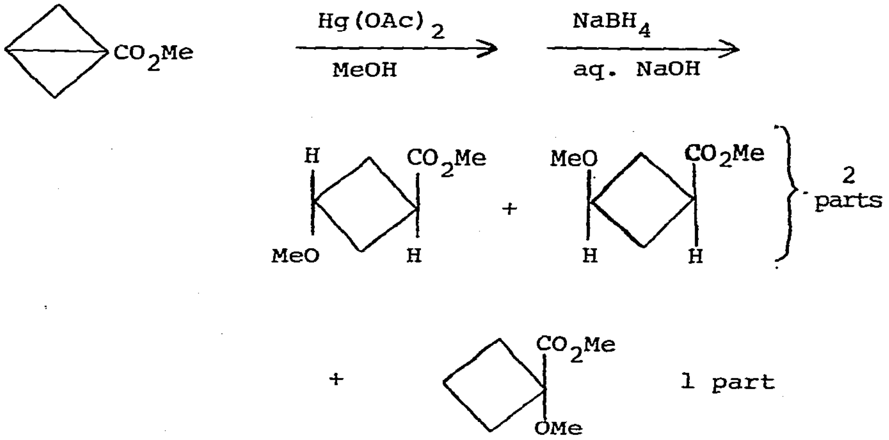


56

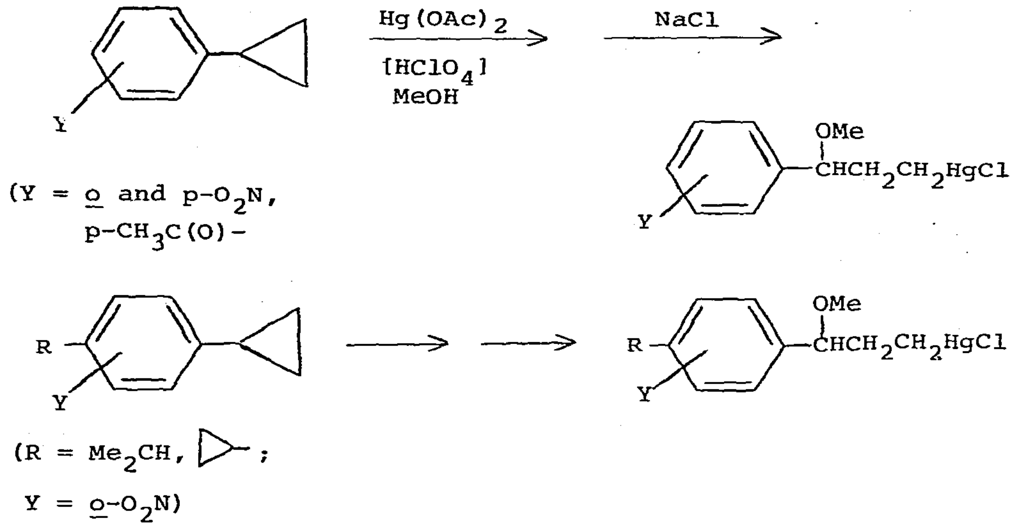


57

The methoxymercuration/demercuration of 1-methoxycarbonylbicyclo[1.1.0]butane has been examined by Russian workers (79):



Nitro- and acetyl-substituted phenylcyclopropanes underwent mercuration with mercuric acetate only in the presence of perchloric acid (61):

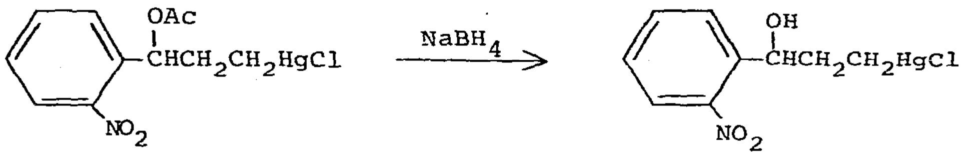


(Y = o and p-O_2N, p-$CH_3C(O)$-

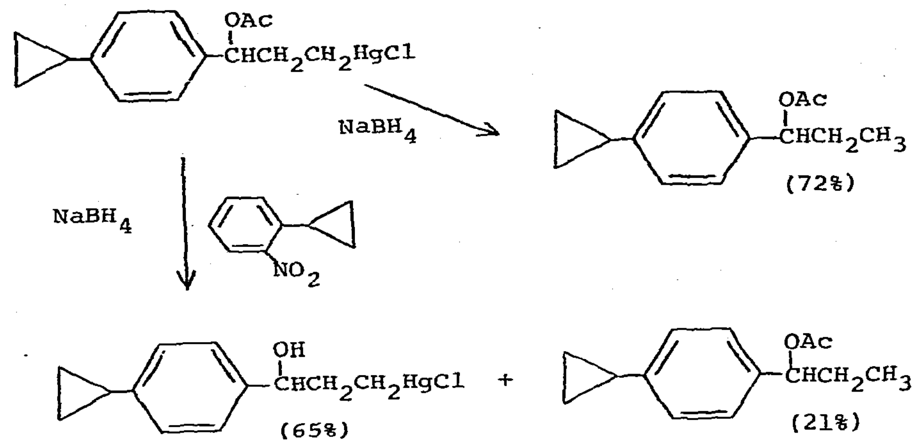
(R = Me_2CH, ; Y = o-O_2N)

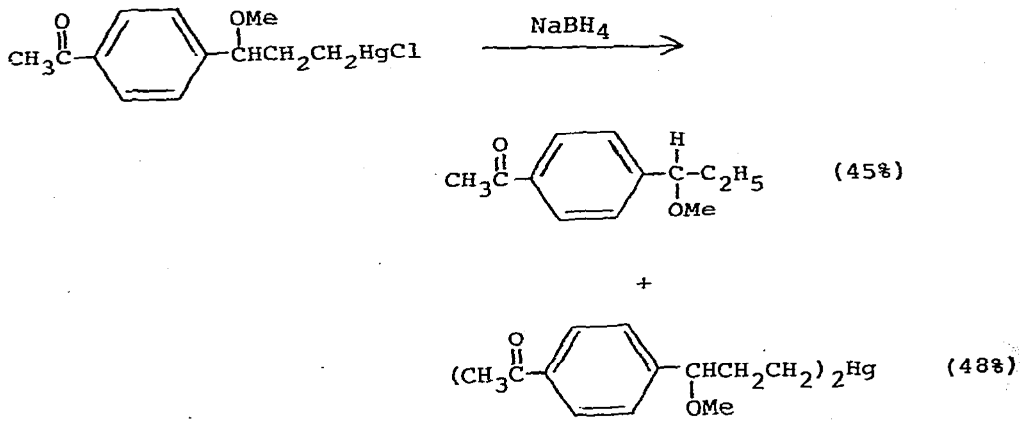
2,4-Dinitrophenylcyclopropane did not react with mercuric acetate even in the presence of perchloric acid.

Demercuration of the nitro-substituted methoxymercuration products proceeded normally, albeit at a rather slow rate. The corresponding acetoxymercuration products, however, reacted with sodium borohydride to give reduction of the acetoxy group rather than reduction of the C-Hg bond, e.g.:

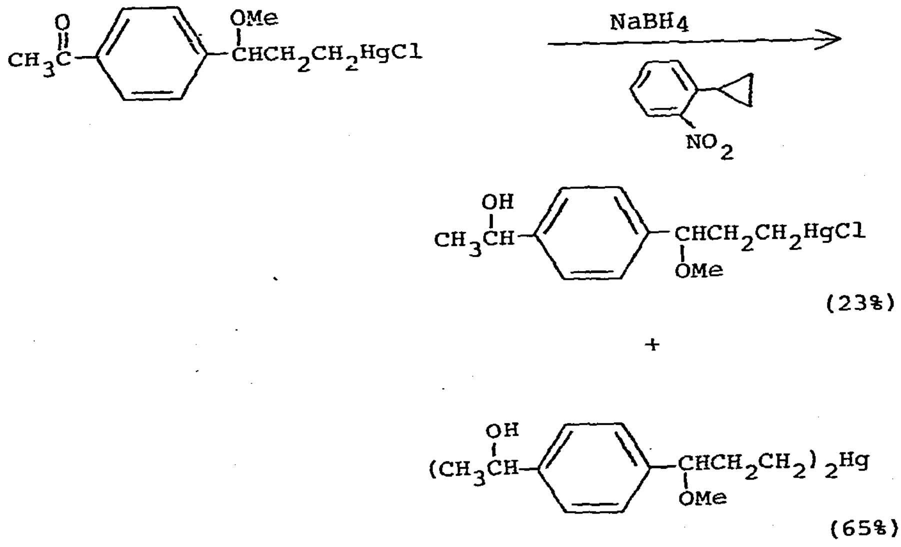


This inhibition of the Cl-Hg bond reduction reaction was atributed to intermolecular coordination of the nitro function to mercury, which either blocked BH_4^- attack at mercury or decreased its rate to such an extent that the reduction of the acetoxy group occurred instead. In support of this idea, it was found that the reduction of such mercurials which did not contain a nitro substituent could be inhibited in part by adding a molar equivalent of *o*-nitrophenylcyclopropane to the reaction mixture:



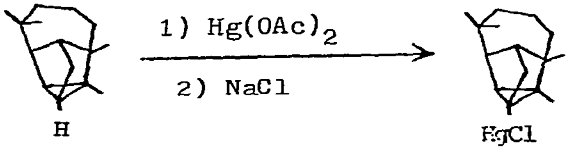


but:



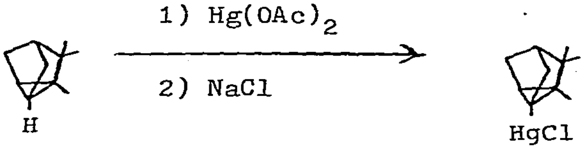
As the authors point out, this ability of nitroaromatics to inhibit $NaBH_4$ reduction of the Hg-Cl function in RHgCl-type mercurials provides the potential for selective reduction of organic functional groups in chloromercuri derivatives of functional organic compounds. This interesting observation merits further attention.

The oxymercuration of longicyclene, 58, proceeded anomalously, giving the cyclopropylmercurial 59 in 50% yield after NaCl work-up (80):



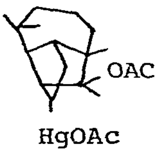
58 59

Lithium aluminum hydride reduction of 59 gave 58, its reaction with bromine in pyridine the corresponding bromide. Tricyclene 60 reacted similarly:



60

It was suggested that these mercurials were formed by HOAc elimination from the original acetoxymercuration product, 61 in the case of 58.



61

D. Aromatic Compounds

Although Hg(II)-arene complexes had been proposed as intermediates in the aromatic mercuration reaction, none had been isolated prior to 1978. Damude and Dean (81) have remedied this situation by preparing such complexes in SO_2 solution and in the solid state:

$$Hg(SbF_6)_2 + 2\ \text{arene} \xrightarrow{\text{liq.}SO_2} Hg(SbF_6)_2 \cdot 2\ \text{arene}$$

$$HgF(AsF_6) + 2\ \text{arene} \xrightarrow{\text{liq.}SO_2} Hg(AsF_6)_2 \cdot 2\ \text{arene} + HgF_2\ (s)$$

Such complexes in which the arene is pentamethylbenzene (yellow), durene (yellow), mesitylene (yellow), p-xylene (pale yellow), toluene (colorless) and benzene (colorless) were isolated as the pure solids in the case of $Hg(SbF_6)_2 \cdot 2$ arene. These hydrolyze slowly in moist air. In liquid sulfur dioxide solution they readily exchange the complexed arene for free arene present in excess in solution and the following equilibria were established:

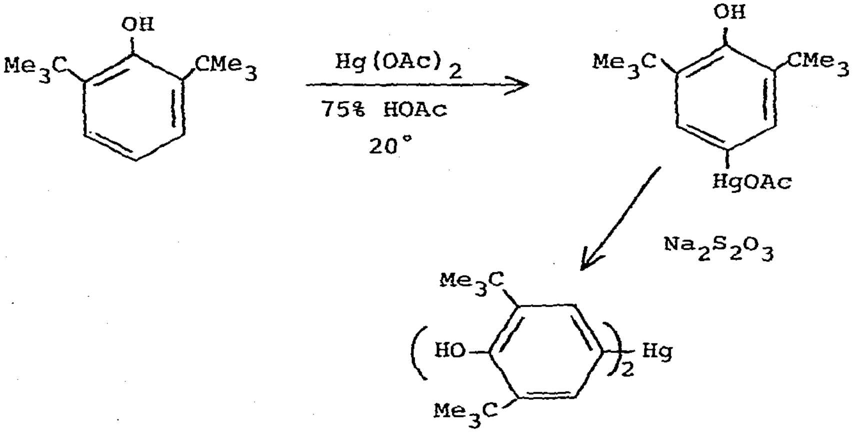
$$Hg^{2+} + C_6H_6 \xrightleftharpoons{308K} Hg(C_6H_6)^{2+} \qquad K_1 \sim 5 \times 10^8\ \text{l.mol}^{-1}$$

$$Hg(C_6H_6)^{2+} + C_6H_6 \rightleftharpoons Hg(C_6H_6)_2^{2+} \qquad K_2$$

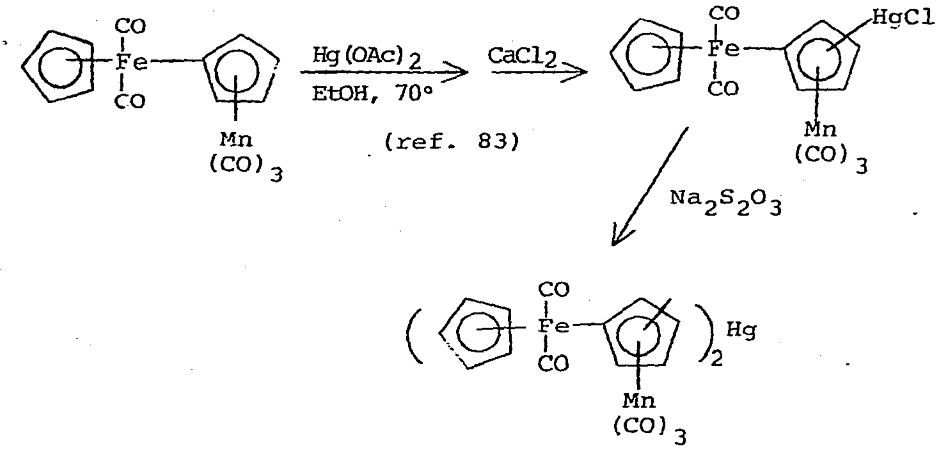
$$(K_1/K_2 = 120)$$

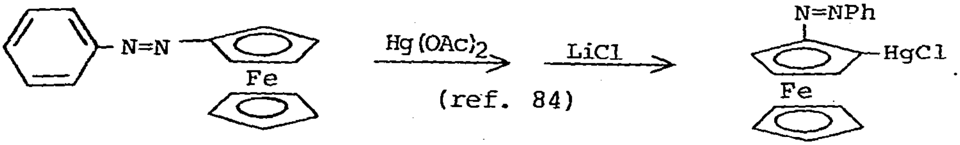
The bis(hexamethylbenzene) complex is the most stable. Structural information is not yet available.

Mercuration of the sterically hindered 2,6-di-tert-butylphenol occurs readily (82):

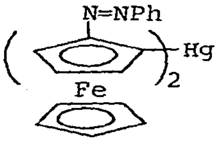


Mercuration reactions of metallocenes have been reported:





Work-up caused partial symmetrization of the product and treatment with sodium thiosulfate solution caused complete symmetrization to 62. Iodine cleavage of the product gave 63 which could in turn be mercurated.



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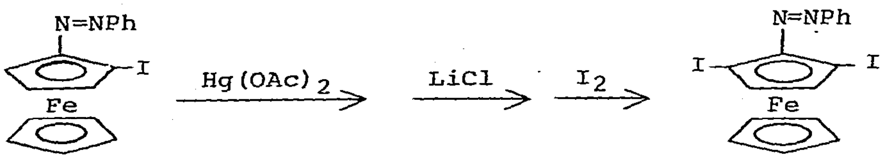

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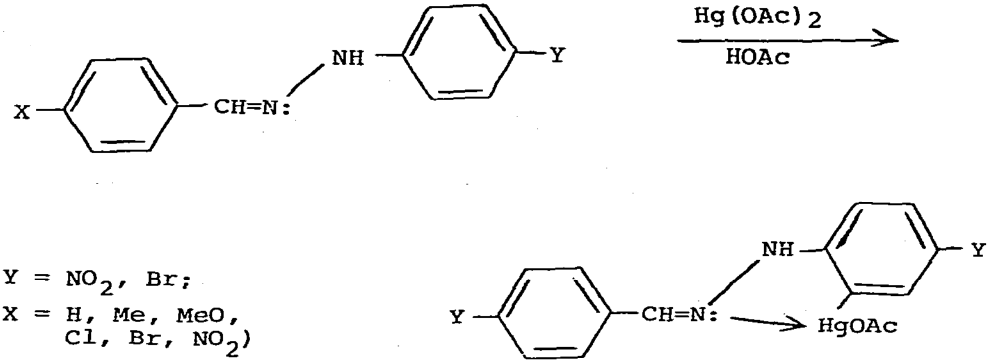
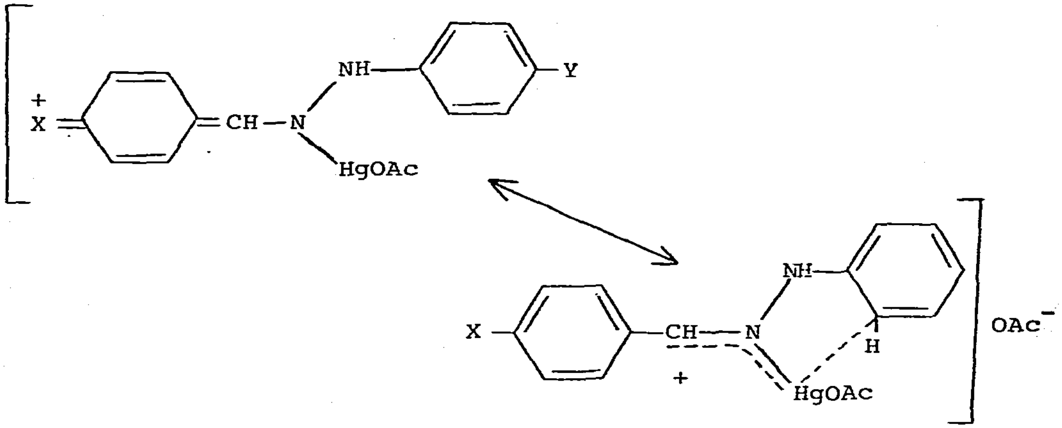
The ortho-mercuration of phenylhydrazones has received further attention with respect to mechanism (85). Only when Y



($Y = NO_2$, Br;
X = H, Me, MeO,
Cl, Br, NO_2)

= NO_2 or Br is this reaction observed; with other aromatic aldehyde phenylhydrazones (e.g., Y = H, MeO, Me (_o_ isomer)) mixtures of red resins and $Hg_2(OAc)_2$ were obtained. The results of kinetic, selectivity and substituent effect studies of the _ortho_ mercuration reaction were interpreted in terms of a transition complex, _64_, which is stabilized by delocalization as shown and which is on the pathway to ortho-metallation.



_64_

Forcing conditions were required to mercurate polyfluoroaromatic compounds which are rather resistant to electrophilic attack (86), e.g.:

$$\begin{tikzcd} C_6F_5H + Hg(O_2CCF_3)_2 + CF_3SO_3H \arrow[r, "73\,^\circ C"] & C_6F_5HgO_3SCF_3 + 2\ CF_3CO_2H \arrow[d, "HCl"] \\ & C_6F_5HgCl \end{tikzcd}$$

In the absence of trifluoromethanesulfonic acid only a negligible amount of product was formed. Numerous examples of such preparations were given (Table 13). The symmetrical mercurials were prepared from the crude mercuration products by treatment with bromide ion:

$$2\ ArHgO_3SCF_3 + 4\ Br^- \longrightarrow Ar_2Hg + HgBr_4^{2-} + 2\ CF_3So_3^-$$

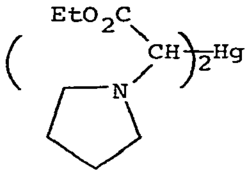
or by heating them in aqueous methanol.

5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS

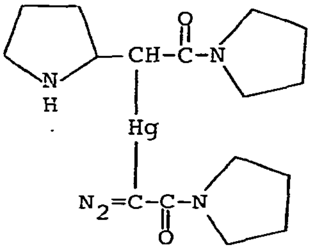
The photodecomposition of mercurated diazoacetic esters in tetrahydrofuran, tetrahydrothiophene and pyrrolidine medium has been studied (87). The major photolysis intermediate is the carbene (65), and 10-20% of the reaction products could be

$$Hg[C(N_2)CO_2Et]_2 \xrightarrow{h\nu} \underset{\underline{65}}{EtO_2C\text{-}\ddot{C}\text{-}Hg\text{-}C(N_2)CO_2Et}$$

accounted for as derived from the carbyne, $EtO_2C\text{-}\dot{C}:$. Both intermediates undergo α C-H insertion into the solvent. Mercury-containing products were obtained when pyrrolidine was used as solvent:

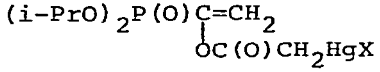


and



Novel phosphono-substituted mercurials were obtained in reactions of mercuric halides with ketene in the presence of triisopropyl phosphite (88):

$$(i\text{-}PrO)_3P + HgX_2 + 2\ CH_2{=}C{=}O \longrightarrow$$



$$(i\text{-}PrO)_2P(O)\underset{OC(O)CH_2HgX}{C}{=}CH_2$$

(X = Cl, Br) 66

(Continued on p.210)

TABLE 13. MERCURATION OF POLYFLUOROARENES WITH MERCURIC TRIFLUOROACETATE/TRIFLUOROMETHANESULPHONIC ACID[a]

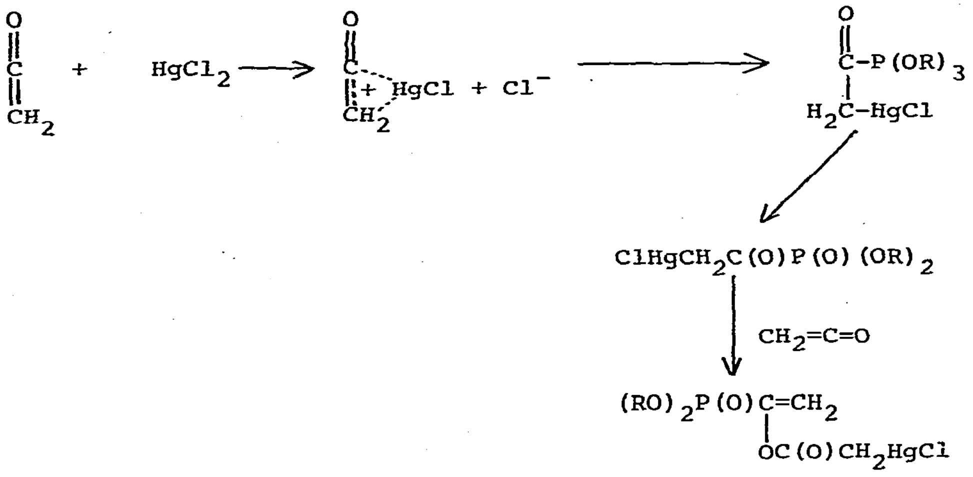
Polyfluoroarene	Temp. (°C)	Time (h)	Product[b] RHgCl	Yield[c] (%)	Product[d] R_2Hg	Yield[c] (%)
C_6F_5H	73	1	C_6F_5HgCl	60	$(C_6F_5)_2Hg$	64
C_6F_5H[e]	73	1	C_6F_5HgCl	ca. 5 (crude)		
$p\text{-MeOC}_6F_4H$	25	0.17	$p\text{-MeOC}_6F_4HgCl$	72	$(p\text{-MeOC}_6F_4)_2Hg$	72
$p\text{-MeC}_6F_4H$	25	144	$p\text{MeC}_6F_4HgCl$	60		
$p\text{-MeC}_6F_4H$	73	0.08	$p\text{-MeC}_6F_4HgCl$	78	$(p\text{-MeC}_6F_4)_2Hg$	76
$m\text{-}H_2C_6F_4$	25	12	$m\text{-HC}_6F_4HgCl$	64		
$o\text{-}H_2C_6F_4$	73	0.25	$o\text{-HC}_6F_4HgCl$	56		
$p\text{-}H_2C_6F_4$	73	1	$p\text{-HC}_6F_4HgCl$	63	$(p\text{-HC}_6F_4)_2Hg$	35
$m\text{-}O_2NC_6F_4H$	73	12	$m\text{-}O_2NC_6F_4HgCl$	50		
$m\text{-}O_2NC_6F_4H$	73	168			$(m\text{-}O_2NC_6F_4)_2Hg$	70[f]
$o\text{-}O_2NC_6F_4H$	73	18	$o\text{-}O_2NC_6F_4HgCl$	14		
$o\text{-}O_2NC_6F_4H$	73	72			$(o\text{-}O_2NC_6F_4)_2Hg$	70
$p\text{-BrC}_6F_4H$	73	18	$p\text{-BrC}_6F_4HgCl$	80		
$p\text{-BrC}_6F_4H$	73	6			$(p\text{-BrC}_6F_4)_2Hg$	73
$m\text{-BrC}_6F_4H$	73	1.5	$m\text{-BrC}_6F_4HgCl$	73		

m-BrC$_6$F$_4$H	73	4.5			(m-BrC$_6$F$_4$)$_2$Hg	64
o-BrC$_6$F$_4$H	73	24	o-BrC$_6$F$_4$HgCl	78		
o-BrC$_6$F$_4$H	73	5.5			(o-BrC$_6$F$_4$)$_2$Hg	52
p-HOC$_6$F$_4$H	25	0.03	p-HOC$_6$F$_4$HgCl	31[g]	(p-HOC$_6$F$_4$)$_2$Hg	73
p-H$_2$NC$_6$F$_4$H	25	0.03	p-H$_2$NC$_6$F$_4$HgCl	69	(p-H$_2$NC$_6$F$_4$)$_2$Hg	71
m-HO$_2$CC$_6$F$_4$H	73	3	m-HO$_2$CC$_6$F$_4$HgCl	79		
(p-HC$_6$F$_4$)$_2$	73	18	p-(p-HC$_6$F$_4$)C$_6$F$_4$HgCl	41		
1,3,5-H$_3$C$_6$F$_3$	25	0.03	3,5-H$_2$C$_6$F$_3$HgCl	61		
C$_6$H$_2$BrF$_3$[h]	73	0.5	C$_6$HBrF$_3$HgCl[h]	59		
C$_6$H$_2$BrF$_3$[i]	73	3	C$_6$HBrF$_3$HgCl[i]	49		

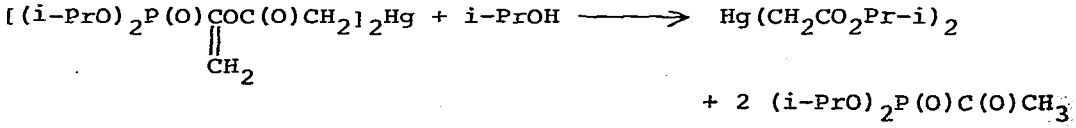
---

[a] Mol. ratio 1:2. [b] After treatment of the product with HCl. [c] Yield of analytically pure product based on mercuric oxide. [d] After treatment of the product with NaBr. [e] In both CF$_3$CO$_2$H and CF$_3$CO$_2$H:H$_2$O = 10:1, v/v. No CF$_3$SO$_3$H added. [f] Yield based on m-O$_2$NC$_6$F$_4$H, as excess of mercurating agent used. [g] After two recrystallizations. One recrystallization gives 52% of slightly impure product. [h] 2-Bromo-1,3,5-trifluorobenzene giving 3-bromo-2,4,6-trifluorophenylmercuric chloride. [i] 1-Bromo-2,4,5-trifluorobenzene giving 3-bromo-2,5,6-trifluorophenylmercuric chloride.

The following reaction course was suggested:



Mercurials of type 66 were symmetrized by the action of triphenylphosphine and the symmetrical mercurials were found to react with alcohols:



$$[(i\text{-}PrO)_2P(O)\underset{\underset{CH_2}{\|}}{C}OC(O)CH_2]_2Hg + i\text{-}PrOH \longrightarrow Hg(CH_2CO_2Pr\text{-}i)_2 + 2\ (i\text{-}PrO)_2P(O)C(O)CH_3$$

The carbanion derived from benzyhydryl cyanide displaces chloride in $Hg(C{\equiv}CCl)_2$ (89):

$$Hg(C{\equiv}CCl)_2 + 2\ Ph_2\bar{C}CN \xrightarrow{DME} Hg(C{\equiv}C\text{-}CPh_2CN)_2 + 2\ Cl^-$$

More a suprising chemical curiosity than a useful synthetic reaction is the fluorination of dimethylmercury at -78°C with elemental fluorine diluted with helium (90). The yield of $(CF_3)_2Hg$ was only 6.5% and cleavage products predominated:

$$(CH_3)_2Hg + F_2/He \xrightarrow[5\ days]{-78°C} Hg(CF_3)_2 + HgF_2 + CF_4 + CHF_3 + CH_2F_2 + CH_3F$$

CH_3HgCF_3 was not present among the products.

6. MERCURY-CARBON BOND REACTIONS

There are a number of procedures for the reduction of olefin solvomercuration products and, more generally, of RHgX-type compounds, to the respective hydrocarbon, RH, and elemental mercury. While alkaline sodium borohydride is the most widely used reagent for this purpose, sodium amalgam was used prior to the advent of $NaBH_4$ and still finds occasional application.

Spanish workers have used alkali metals (Li, Na, K) and magnesium (91,92) as well as calcium amalgam (93) in recent studies. In this procedure the metal is added to the reaction mixture after completion of the olefin solvomercuration step. The organometallic intermediate which is formed is converted to the hydrocarbon by reaction with the excess of the nucleophile used in the olefin solvomercuration, e.g.:

$$\begin{tikzcd}
CH_2{=}CH_2 + PhNH_2 + Hg(OAc)_2 \arrow[r] & PhNHCH_2CH_2HgOAc \arrow[d, "M\ (= Li,\ Na,\ K)"] \\
 & PhNHCH_2CH_2M \arrow[d, "PhNH_2"] \\
 & PhNHCH_2CH_3 \quad (56\text{-}58\%)
\end{tikzcd}$$

An alternate procedure also used involves the isolation of the solvomercuration product prior to its reduction. A large number of examples of such reductions of olefin oxymercuration and aminomercuration products was provided.

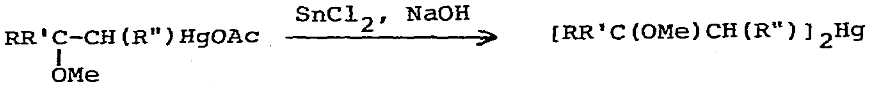
Triethylsilane also reduces $RHgO_2CCF_2$ compounds (94):

$$Ar_2C{=}CHHgO_2CCF_3 \xrightarrow[\substack{CH_2Cl_2,\ CHCl_3 \\ \text{or } CH_3CN}]{Et_3SiH \text{ in}} Ar_2C{=}CH_2 + Hg$$

$$(Ph_2C{=}CH)_2Hg \xrightarrow[CHCl_3]{Et_3SiH,\ CF_3CO_2H} Ph_2C{=}CH_2 + Hg$$

$$Ar_2CHCH_2HgO_2CCF_3 \xrightarrow[\substack{CH_2Cl_2,\ CHCl_3 \\ \text{or } CH_3CN}]{Et_3SiH \text{ in}} Ar_2CHCH_3 + Ar_2C{=}CH_2$$

In contrast to these reductions, the action of sodium stannite on β-alkoxyalkylmercuric acetates resulted in symmetrization (95):



$$\underset{\text{OMe}}{\text{RR'C}}\text{-CH(R")HgOAc} \xrightarrow{\text{SnCl}_2\text{, NaOH}} [\text{RR'C(OMe)CH(R")}]_2\text{Hg}$$

Such symmetrical mercurials were prepared from the methoxymercuration products of ethylene, propene, 2-methylpropene, cis- and trans-2-butene, cyclopentene, 1-hexene, cyclohexene, 1-methylcyclohexene, styrene, 2-phenylpropene, 1,1-diphenylethylene, 1,3-butadiene, 1,3-pentadiene, 1,5-hexadiene, methyl vinyl ether, diallyl ether and 3-oxacyclohexene, as well as from various olefin ethoxymercuration products.

Other types of Hg-C bond cleavage reactions have been examined.

The kinetics of the iodinolysis of substituted arylmercuric chlorides have been studied (96).

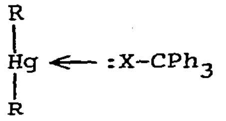
The copper(II) bromide cleavage of $PhCH(OMe)CH_2HgOAc$ has been studied in spin-trapping experiments with Me_3CNO in acetonitrile (97). Although previous workers have given evidence for a mechanism involving alkyl radicals, only weak ESR signals were observed. In was conjectured that either the free alkyl radical concentrations are quite low or that the alkyl radicals are not completely free.

The action of triarylmethyl perchlorates on dialkylmercurials containing β hydrogen results in Hg-C cleavage:

$$(RCH_2CH_2)_2Hg + Ar_3C^+ClO_4^- \xrightarrow[\text{or } CH_3CN \\ 25°C]{\text{dichloroethane}} RCH_2CH_2HgClO_4 + RCH{=}CH_2$$

(R = H, Me;
Ar = Ph, p-MeC_6H_4)

The rates of these reactions have been studied by proton NMR spectroscopy (98). The hydride abstraction from the β position by the Ar_3C^+ cation occurs synchronously with rupture of the Hg-C bond (an E_E2 mechanism). In the case of triarylmethyl halides, initial coordination with the mercurial, as in 67, was



$$\begin{array}{l} \text{R} \\ | \\ \text{Hg} \leftarrow :\text{X-CPh}_3 \\ | \\ \text{R} \end{array}$$

67

suggested, with subsequent ionization of the C-X bond thus being facilitated.

Radical decomposition of dibenzylmercury in toluene medium at temperatures of 130-170°C has been investigated in detail by Jackson and O'Neill (99):

$$(PhCH_2)_2Hg \longrightarrow PhCH_2CH_2Ph + Hg \text{ (+ traces of } PhCH{=}CHPh \text{ and } PhCH_2CHPhCH_2Ph)$$

In the temperature range 130-160°C first order kinetics were followed, with $\log_{10}A = 16.0 \pm 0.3$ and $E = 38.5 \pm 0.5$ kcal/mol. The following scheme was suggested:

$$\begin{tikzcd}(PhCH_2)_2Hg \arrow[r, "\text{rate determining}"] & PhCH_2\cdot + PhCH_2Hg\cdot \arrow[d] \\ & Hg + PhCH_2\cdot\end{tikzcd}$$

$$2\ PhCH_2\cdot \longrightarrow PhCH_2CH_2Ph$$

$$PhCH_2\cdot + PhCH_2CH_2Ph \longrightarrow PhCH_3 + Pn\dot{C}HCH_2Ph$$

$$\begin{tikzcd}Ph\dot{C}HCH_2Ph + PhCH_2\cdot \arrow[r] \arrow[dr] & PhCH{=}CHPh + PhCH_3 \\ & PhCH_2CHPhCH_2Ph\end{tikzcd}$$

Radical polymerization of vinyl monomers such as methacrylate and acrylate esters may be effected under aerobic conditions using $i\text{-}Pr_2Hg/SnCl_4\cdot 5H_2O$ as the initiator system. Stable polymeric coatings which were mold-resistant were produced (100).

7. MERCURY-FUNCTIONAL MERCURIALS

A. Mercurials with Halogen and Oxy Substituents

The formation constants of CH_3HgCl, CH_3HgBr and CH_3HgNO_3 in aqueous and organic phases have been determined by liquid-liquid extraction studies in the systems o-xylene/1.0M (H, Na)

(Br,Cl,NO_3)(aq) and o-xylene/2,5$\underline{M}$ (H,Na)(Br,Cl,NO_3)(aq) (101):

$MeHg^+ + Cl^- \rightleftharpoons MeHgCl(aq)$ log K = 5.50
$MeHg^+ + Cl^- \rightleftharpoons MeHgCl(org)$ 6.59
$MeHg^+ + NO_3^- \rightleftharpoons MeHgNO_3(org)$ -1.21
$MeHg^+ + Br^- \rightleftharpoons MeHgBr(aq)$ 6.60
$MeHg^+ + Br^- \rightleftharpoons MeHgBr(org)$ 8.30
$MeHg^+ + 2Br^2 \rightleftharpoons MeHgBr_2^-(aq)$ 5.98

This gives distribution constants:

$MeHgCl(aq) \rightleftharpoons MeHgCl(org)$ log K(D) = 1.09
$MeHgBr(aq) \rightleftharpoons MeHgBr(org)$ log K(D) = 1.69

Another group has determined distribution constants for MeHgCl, EtHgCl and n-PrHgCl between aqueous 1 mol dm^{-3} (H, Na)Cl and benzene: K(D) = $10^{1.04}$, $10^{1.60}$ and $10^{2.20}$, respectively (102).

The symmetrization of MeHgCl to give Me_2Hg can be effected by ethylenediamine in $CDCl_3$ and by tertiary phosphines in dichloromethane, with the effectiveness of the latter decreasing in the order: $Et_3P > Me_2PhP > MePh_2P > Ph_3P$ (103). These homogeneous systems were studied by NMR. Thiols did not cause such symmetrization.

The equilibrium constants for the interaction of $MeHg^+$ and water and some carboxylic acids have been determined by a potentiometric method (104), e.g.:

$MeHg^+ + H_2O \rightleftharpoons MeHgOH + H^+$ log K = -4.686
$2\ MeHg^+ + H_2O \rightleftharpoons (MeHg)_2OH^+ + H^+$ -1.725
$MeHgOH(s) \rightleftharpoons MeHg^+ + OH^-$ (in H_2O) - 13.66
$MeHg^+ + OAc^- \rightleftharpoons MeHgOAc$ 3.204
$MeHg^+ + O_2CH^- \rightleftharpoons MeHgO_2CH$ 2.681
$MeHg^+ + O_2CCH(NH_2)CHMe_2^- \rightleftharpoons MeHgO_2CCH(NH_2)CHMe_2$ 7.268
$MeHg^+ + O_2CCH(NH_2)Me^- \rightleftharpoons MeHgO_2CCH(NH_2)Me$ 7.516

Also studied has been the complex formation between $CH_3Hg(II)$ and ethylenediaminetetraacetic acid (105).

The Hg(II) salt of nitrodifluoroacetic acid, $Hg(O_2CCF_2NO_2)_2$, has been prepared (106). Spectroscopic studies suggested that there is a donor/acceptor interaction between a methyl substituent (probably NO_2) and mercury. Reaction of this salt with organic halides, RX (X = Br, I), in acetonitrile gave esters, $O_2NCF_2CO_2R$. Decarboxylation of $Hg(O_2CCF_2NO_2)_2$ occurred in basic aqueous medium, giving HCF_2NO_2.

An interesting mercurial has been prepared by the reaction of elemental mercury with perfluoro-t-butyl hypochlorite (107):

$$(CF_3)_3COCl + Hg \xrightarrow{CCl_3F} (CF_3)_3COHgCl$$

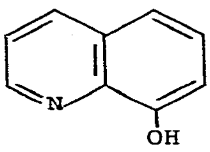
The reactions of this product, a stable white solid, were studied:

$$\begin{array}{lll}
(CF_3)_3COHgCl & + \; CH_3I \longrightarrow & (CF_3)_3COCH_3 \\
 & + \; CF_3SCl \longrightarrow & (CF_3)_3COSCF_3 \\
 & + \; CF_3C(O)Br \longrightarrow & (CF_3)_3COC(O)CF_3 \\
 & + \; CF_3C(O)SCl \longrightarrow & (CF_3)_3COSC(O)CF_3 \\
 & & \downarrow \\
 & & (CF_3)_3COC(O)CF_3 + S_8 \\
 & + \; Me_3SiCl \longrightarrow & (CF_3)_3COSiMe_3 \\
 & + \; Me_3SiH \longrightarrow & (CF_3)_3COSiMe_3 \\
 & + \; CH_3C(O)Cl \longrightarrow & (CF_3)_3COC(O)CH_3 \\
 & + \; (CF_3)_2C{=}NH \longrightarrow & (CF_3)_2C{=}NCl
\end{array}$$

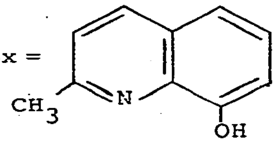
Organomercuric quinolin-8-olates have been prepared (108):

$$RHgOH + H(ox\ or\ Meox) \longrightarrow RHg(ox\ or\ Meox) + H_2O$$

(H−ox=



H−Meox =



R = Me, Ph)

$$Ar_fHgCl + Tl(ox) \longrightarrow Ar_fHg(ox) + TlCl$$

$(Ar_f = C_6F_5,\ p\text{-}HC_6F_4,\ p\text{-}MeOC_6F_4)$

Detailed UV and mass spectral and solution molecular weight studies were carried out and these supported chelate, rather unidentate O-bonding of the ox substituent. Except for the MeHg compound, all appeared to be partly associated in chloroform and carbon tetrachloride solution.

B. Mercurials with Sulfur, Selenium and Tellurium Substituents

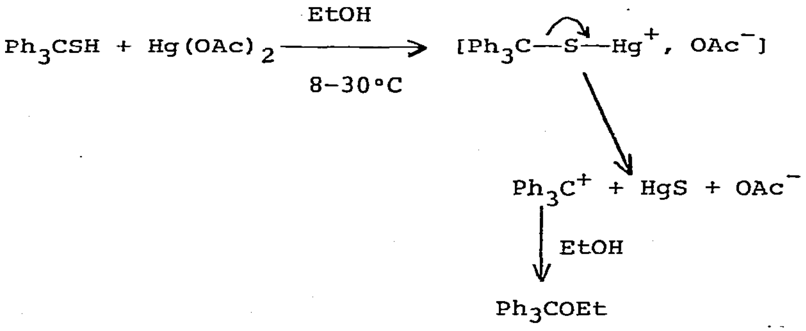
A series of RSHgX compound (R = Et, t-Bu; X = Cl, Br; R = Me, Et, n-Pr, n-Bu; X = OAc) has been prepared (109):

$$\mathrm{RSH} + \mathrm{HgX_2} \xrightarrow{\mathrm{EtOH}} \mathrm{RSHgX} + \mathrm{HX}$$

$$(\mathrm{X} = \mathrm{Cl}, \mathrm{Br})$$

$$(\mathrm{RS})_2\mathrm{Hg} + \mathrm{Hg(OAc)_2} \xrightarrow{\mathrm{H_2O}} \mathrm{RSHgOAc} + \mathrm{CH_3C(O)SR}$$

These RSHgOAc form crystalline adducts with pyridine of 1:1 stoichiometry. Vibrational spectra were measured and used in a discussion of structure. Their reactions with imidazole and related ligands were investigated (110). When a very stable carbonium ion, R^+, can be formed, RSHgOAc compounds are quite unstable (111):



The benzyl analog, $PhCH_2SHgOAc$, did not undergo such solvolytic decomposition until 90-100°C, and $Me_2CHCH_2SHgOAc$ is stable.

PhHgSR derivatives have served in the separation of thiols, RSH, by thin layer chromatography (112).

The formation constant of RHg(II) derivatives of L-cysteine were determined by liquid-liquid distribution (102):

$$\mathrm{RHgCl} + \mathrm{R'SH} \rightleftharpoons \mathrm{RHgSR'} + \mathrm{H^+} + \mathrm{Cl^-}$$

$$(\mathrm{R'} = \mathrm{HO_2CCH(NH_2)CH_2})$$

$$K = \frac{(RHgSR')(H^+)(Cl^-)}{(RHgCl)(R'SH)}$$

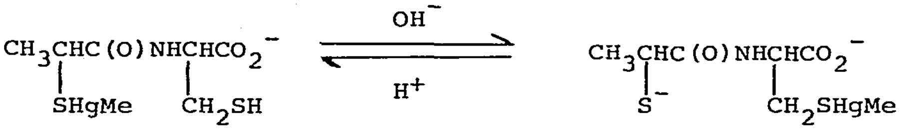
For CH_3HgCl $K = 10^{1.71}$

$EtHgCl$ $K = 10^{1.55}$

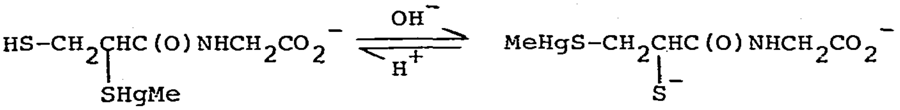
$n\text{-}PrHgCl$ $K = 10^{1.49}$

The distribution of $CH_3Hg(II)$ between the chloride and sulfhydryl ligands at physiological and at stomach pH has been studied (113).

The mercury(II) derivative of trifluoromethylselenol, $Hg(SeCF_3)_2$, reacts with $CF_3SC(O)Br$ at 130°C to give $CF_3SC(O)-SeCF_3$ and $CF_3SeHgBr$ (114). The binding affinity of $CH_3Hg(II)$ toward selenium-containing ligands, $HSeCH_2CH_2NH_3^+$, $(H_3N^+CH_2CH_2Se)_2$, $HSeCH_2CH(CO_2^-)NH_3^+$ and $(H_3N^+CH(CO_2^-)CH_2Se)_2$, has been studied by proton MMR spectroscopy (115). For a number of common biological groups the binding affinity toward $CH_3Hg(II)$ decreases in the order:$SeH>SH>Se\text{-}Se>NH_2>S\text{-}S$, $SeCH_3$, SCH_3. Also examined were $CH_3Hg(II)$ complexes of peptides containing two sulfhydryl groups, 2-mercapto-propionyl-L-cysteine and 2,3-dimercapto-propionylglycine. pH-Dependent equilibria were found to obtain for the 1:1 complexes:



$$CH_3\underset{SHgMe}{\underset{|}{C}}HC(O)NH\underset{CH_2SH}{\underset{|}{C}}HCO_2^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} CH_3\underset{S^-}{\underset{|}{C}}HC(O)NH\underset{CH_2SHgMe}{\underset{|}{C}}HCO_2^-$$

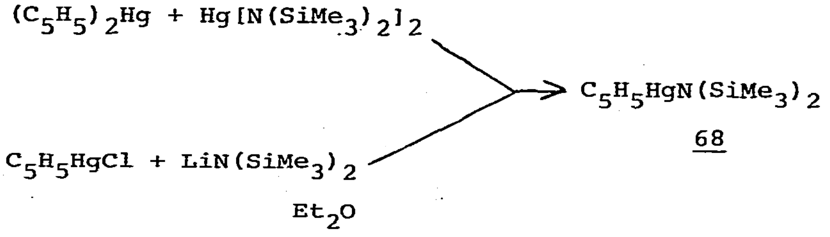


$$HS\text{-}CH_2\underset{SHgMe}{\underset{|}{C}}HC(O)NHCH_2CO_2^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} MeHgS\text{-}CH_2\underset{S^-}{\underset{|}{C}}HC(O)NHCH_2CO_2^-$$

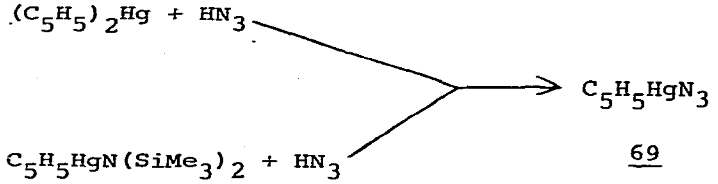
Organotellurium-mercury(II) halide complexes of type $R_2Te\cdot HgX_2$ (R = Ph, $p\text{-}EtOC_6H_4$; X = Cl, Br, I), $\alpha\text{-}Me_2TeI_2\cdot HgBr_2$, $Ph_2Hg(Me_2TeI_2)_2$, $(p\text{-}EtOC_6H_4Te)_2Hg$, $p\text{-}EtOC_6H_4TeHgCl$ and $R_2Te_2\cdot HgX_2$ (R = $p\text{-}EtOC_6H_4$; X - Cl, Br, I) have been studied by ^{125}Te Mössbauer, infrared and Raman spectroscopy (116).

C. Mercurials with Nitrogen Substituents

A cyclopentadienylmercuric amide and the azide have been prepared (117):



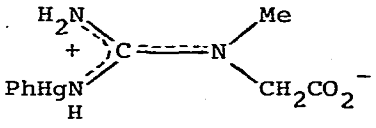
68



69

In 68 and 69 the C_5H_5 substituents are monohapto according to their vibrational spectra. The proton NMR and the mass spectra of these compounds also were studied.

PhHg(II) derivatives of creatine, 70, and creatinine, 71, 72, were prepared by Canty et al. (118).

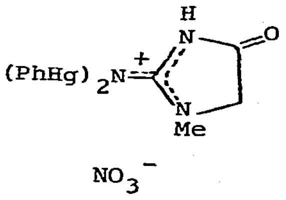


70

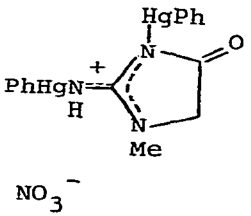
$[PhHg(H_2creat)][NO_3] \cdot \frac{1}{2}H_2O$ 71

$[(PhHg)_2(Hcreat)][NO_3]$ (two forms) 72

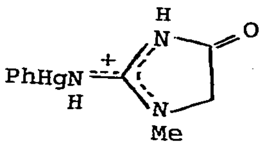
72 could be either 73 or 74, and the structure of one form was determined by X-ray diffraction to be 74 (Fig. 1). 71 has the structure 75 (119)



73



74



75

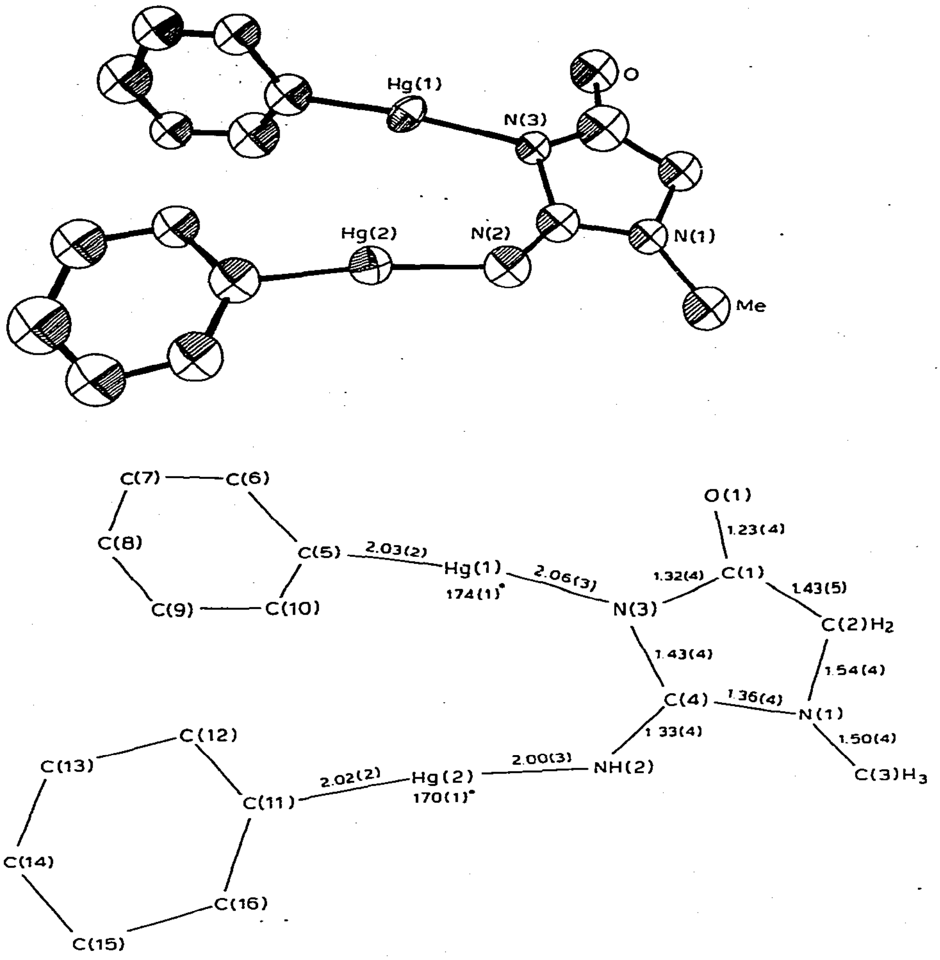
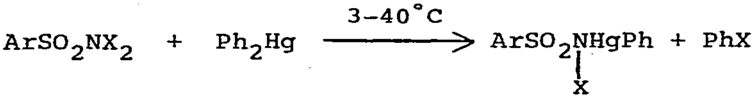


Figure 1. Structure of the cation $[(PhHg)_2Hcreat]^+$ in $[(PhHg)_2Hcreat][NO_3]$ (<u>1a</u>) and selected structural parameters in the cation (<u>1b</u>). From A.J. Canty, M. Fyfe and B.M. Gatehouse, Inorg. Chem., 17 (1978) 1467.

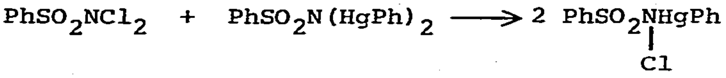
N-Phenylmercurisulfonamides have been prepared by Russian workers (120):



$$ArSO_2NX_2 + Ph_2Hg \xrightarrow{3-40^\circ C} ArSO_2\underset{\displaystyle X}{\underset{|}{N}}HgPh + PhX$$

$(X = Cl, Br;$
$Ar = Ph, p\text{-}MeC_6H_4, p\text{-}ClC_6H_4)$

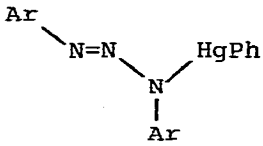
$$\mathrm{ArSO_2NX_2 + 2\ Ph_2Hg \longrightarrow ArSO_2N(HgPh)_2 + 2\ PhX}$$



$$\mathrm{PhSO_2NCl_2 \quad + \quad PhSO_2N(HgPh)_2 \longrightarrow 2\ PhSO_2\underset{\displaystyle Cl}{\underset{|}{N}}HgPh}$$

The thermolysis of the monomercurated compounds gave insoluble, polymeric products, $(\mathrm{ArSO_2NHg})_x$, which were found to be resistant to aqueous acid and alkalis and to carboxylic acids.

The action of phenylmercuric hydroxide or acetate on 1,3-diaryl-1-triazenes gave mercurated products (121,122), 76:



76

(Ar = 2-$\mathrm{XC_6H_4}$ with X = F, Cl, Me, $\mathrm{O_2N}$; 3-$\mathrm{XC_6H_4}$, with X = Cl, F and $\mathrm{O_2N}$; 4-$\mathrm{XC_6H_4}$, with X = F, Cl, Me, $\mathrm{O_2N}$)

IR and proton NMR studies showed that these air- and moisture-stable compounds have monodentate structures as shown in 76, but that they undergo rapid $1 \rightleftharpoons 3$ site exchange. The fluorophenyl derivatives have been the subject of a temperature-dependent ^{19}F NMR study which provided confirmation of this fluxional behavior (122).

D. B-Mercurated Carboranes

B-Mercurated carboranes serve as reagents for the preparation of carboranes containing B-Tl (123, 124) and B-As bonds (125):

$$\mathrm{(C_2H_2B_{10}H_9\text{-}9)_2Hg + (CF_3CO_2)_3Tl \longrightarrow 9\text{-}(CF_3CO_2)_2Tl\text{-}B_{10}H_9C_2H_2}$$
$$\mathrm{+\ 9\text{-}CF_3CO_2Hg\text{-}B_{10}H_9C_2H_2}$$

(with o- and m-carborane isomers)

$$\mathrm{(C_2H_2B_{10}H_9\text{-}9)_2Hg + AsCl_3 \longrightarrow 9\text{-}Cl_2As\text{-}B_{10}H_9C_2H_2}$$
$$\mathrm{+\ 9\text{-}ClHg\text{-}B_{10}H_9C_2H_2}$$

(o- and m- isomers)

B-Mercurated carboranes may also be used in the preparation of carboranyl derivatives of tin, antimony and sulfur (126):.

$$(C_2H_2B_{10}H_9\text{-}9)_2Hg + SnCl_2 \longrightarrow (C_2H_2B_{10}H_9\text{-}9)_2SnCl_2 + Hg$$

(o- and m- isomers)

$$(C_2H_2B_{10}H_9\text{-}9)_2Hg + SbCl_3 \longrightarrow 9\text{-}Cl_2Sb\text{-}B_{10}H_9C_2H_2$$

(o- and m- isomers)

$$+ 9\text{-}ClHg\text{-}B_{10}H_9C_2H_2$$

$$(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2Hg + S_8 \xrightarrow{350°C} (m\text{-}C_2H_2B_{10}H_9\text{-}9)_2S_2 + Hg$$

$$(m\text{-}C_2H_2B_{10}H_9\text{-}9)_2Hg + S_8 \xrightarrow[115°C]{I^-,\ DMF} m\text{-}C_2H_2B_{10}H_9\text{-}S\text{-}Hg\text{-}B_{10}H_9C_2H_2$$

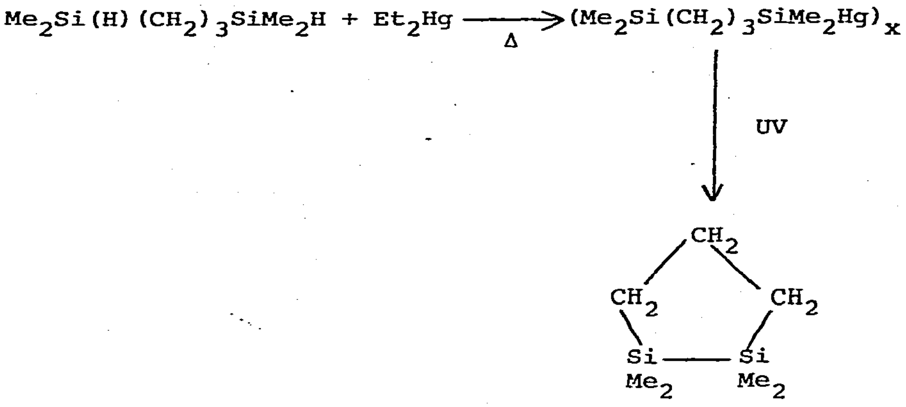
The Raman spectra of B-mercurated carboranes (o- and m-$C_2H_2B_{10}$-H_9-HgR, with R = Cl, Br, Me, Et, (o- and m-$C_2H_2B_{10}H_9$-9)$_2$Hg) and of C-mercurated o-, m- and p-carboranes have been examined.

Vibrations around 150 cm^{-1} were identified as Hg-carborane stretching modes in which the carborane nucleus behaves as a rigid body pseudoatom (127).

E. Mercurials with Group IV Substituents

A detailed study has been made of the ^{13}C, ^{29}Si and ^{199}Hg NMR spectra of silyl and germyl mercurials of type RHgSiMe$_3$, RHgSiEt$_3$ and RHgGeMe$_3$ (R = alkyl, SiMe$_3$, SiEt$_3$ and GeMe$_3$) (128). Chemical shift and coupling constant data are tabulated and discussed. Tables 14 and 15 bring some of these data.

A silylmercurial has found useful application in the synthesis of a 1,2-disilacyclopentane (129):



$$Me_2Si(H)(CH_2)_3SiMe_2H + Et_2Hg \xrightarrow[\Delta]{} (Me_2Si(CH_2)_3SiMe_2Hg)_x$$

The photochemical or thermal reactions of bis(trimethylsilyl)mercury with hindered diaryl ketones and a number of alkyl

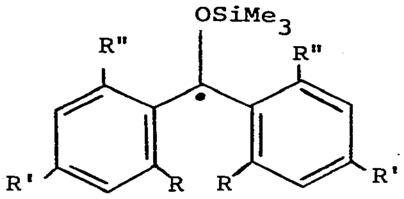
TABLE 14. ^{199}Hg and ^{29}Si Chemical Shifts[a] in Compounds $RHgSiMe_3$ (in ppm) (128)

Compound	R	$\delta(^{199}Hg)$[b]	$\delta(^{29}Si)$[c]
	Me	d	33.0
	Et	d,e	34.0
	Pr	2527	35.2
	Bu	2520	35.0
	i-Pr	2312[f]	34.0
	t-Bu	2172[g]	33.6
	Me_3Si[h]	2927	63.6
	CH_2Cl	d	30.3
	Et_3Si[f]	3278	35.1

---

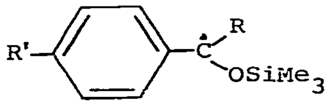
[a] The usual sign convention is used. [b] Relative to a saturated solution of $Hg(NO_3)_2$, ± 2 ppm. [c] Relative to internal TMS, ± 0.3 ppm. [d] Not measured. [e] For $EtHgGeMe_3$ $\delta = 2272$ ppm. [f] For i-$PrHgGeMe_3$ $\delta = 2129$ ppm. [g] For t-$BuHgGeMe_3$ $\delta = 2591$ ppm, for t-Bu_2Hg 1598 ppm. [h] Lit. 64.0 ppm. [i] $(Et_3Si)_2Hg$.

aryl ketones were used to prepare O-silyl ketyls of types 77, 78, 79 and 80 (130). Similar (silylamino)methyl radicals were



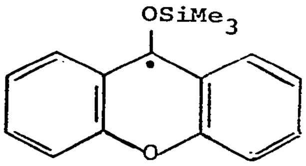
77

R	R'	R"
H	H	H
Me	H	H
MeO	MeO	H
Me	Me	H
Me	Me	Me
Me	Me	t-Bu

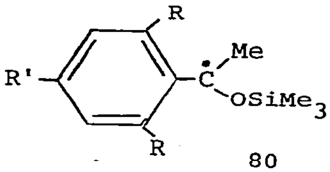


79

R	R'
CF_3	H
CPh_3	H
adamantyl	H
t-Bu	H
t-Bu	Me
t-Bu	t-Bu



78



80

R	R'
H	H
Me	Me
Me	H
Me	t-Bu
Et	H
Et	Et
iPr	H
iPr	iPr
t-Bu	t-Bu

generated by the action of bis(trimethylsilyl)mercury (photo-

(Continued on p.226)

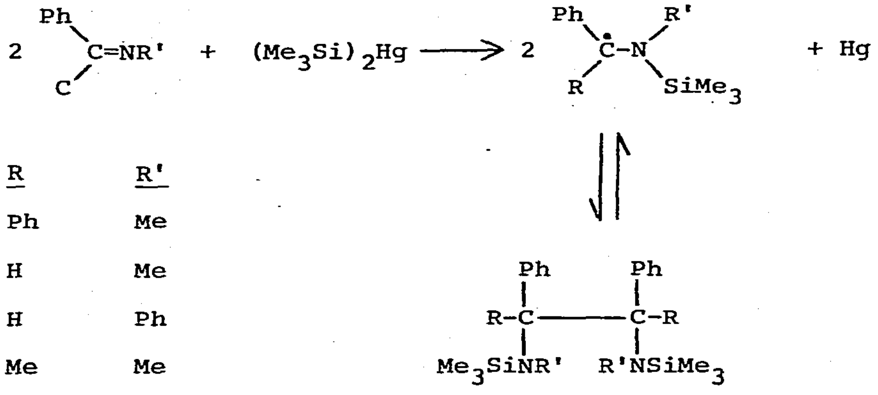
TABLE 15. MERCURY-CARBON AND MERCURY-SILICON COUPLING CONSTANTS IN COMPOUNDS $RHgMMe_3$ (M = Si,Ge) (in Hz). Values in parentheses refer to R_2Hg. Coupling constant values are generally accurate to ± 0.5 Hz. (128)

Compound	R	M	$^1J(Hg-C(1))$	$^2J(Hg-C(2))$	$^2J(Hg-M-C)$	$^1J(Hg-Si)$
	Me	Si	423.4 (689)	-	116.8	1367.0
	Me	Ge	524.3	-	117.9	-
	Et	Si	495.5 (648)	18.3 (25)	109.9	1213.0
	Et	Ge	601.5	25.3	105.3	-
	Pr	Si	497.8 (658)	18.3[a] (26)[b]	112.1	1234.1
	Pr	Ge	597.4	24.1[c]	106.4	-
	Bu	Si	496.8 (656)	18.0[d] (26)[e]	112.1	1225.9
	Bu	Ge	593.3	25.3[f]	109.9	-
	i-Pr	Si	564.7 (633.6)	g (32)	104.4	1084.9 -
	i-Pr	Ge	666.0	g	97.3	-
	t-Bu	Si	611.9 (631)	26.6 (30)	101.5	995.6
	t-Bu	Ge	716.4	22.9	92.7	-

Me_3Si	Si	-	-	93.8	989.6[h]
Me_3Ge	Ge	-	-	96.3	-
CH_2Cl	Si	446.3 (-)	-	132.8	1137.0
CH_2Cl	Ge	573.4	-	132.8	-
Et_3Si	Si[i]	(-) (-)	-	58.0[f]	957.0[h]

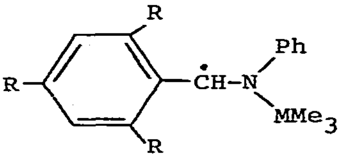
[a] ^3J(Hg-C(3) 91.5. [b] ^3J(Hg-C(3)) 103. [c] ^3J(Hg-C(3)) 103.0 [d] ^3J(Hg-C(3)) 89.3 [e] ^3J(Hg-C(3)) 100. [f] ^3J(Hg-C(3)) 103.5. [g] No coupling observed. [h] ± 2 Hz. [i] $(Et_3Si)_2Hg$. [j] ^3J(Hg-C) 37.8 Hz .

chemical or thermal) on imines (131):



R	R'
Ph	Me
H	Me
H	Ph
Me	Me
H	CH_2Ph

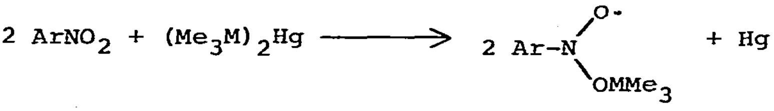
Use of $(Me_3Ge)_2Hg$ in place of the silylmercurial gave the analogous (trimethylgermyl)methyl radicals. More hindered radicals, 81, also were prepared by this route.



81

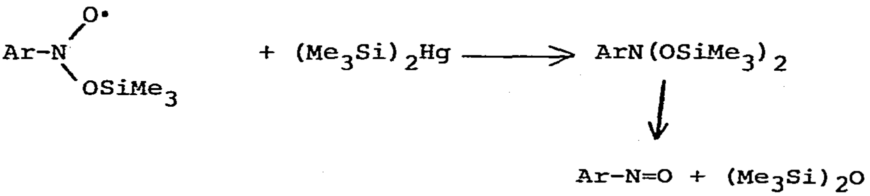
(M = Si, Ge; R = H, Me, Et, i-Pr)

Radicals also were produced in reactions of bis(trimethylsilyl)mercury and bis(trimethylgermyl)mercury with nitroarenes (132):



$$2\ ArNO_2 + (Me_3M)_2Hg \longrightarrow 2\ Ar\text{-}N(O\cdot)(OMMe_3) + Hg$$

An excess of $(Me_3Si)_2Hg$ in this reaction produces silyloxyaminyls:

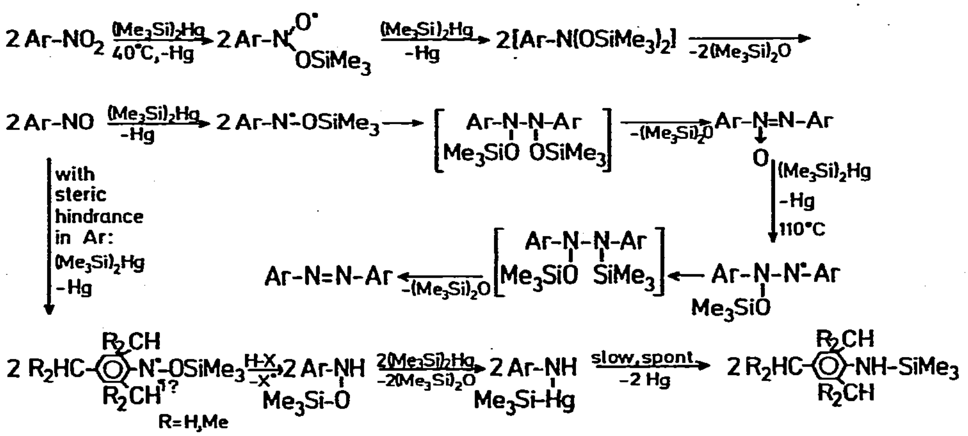


$$Ar\text{-}N(O\cdot)(OSiMe_3) + (Me_3Si)_2Hg \longrightarrow ArN(OSiMe_3)_2 \longrightarrow Ar\text{-}N{=}O + (Me_3Si)_2O$$

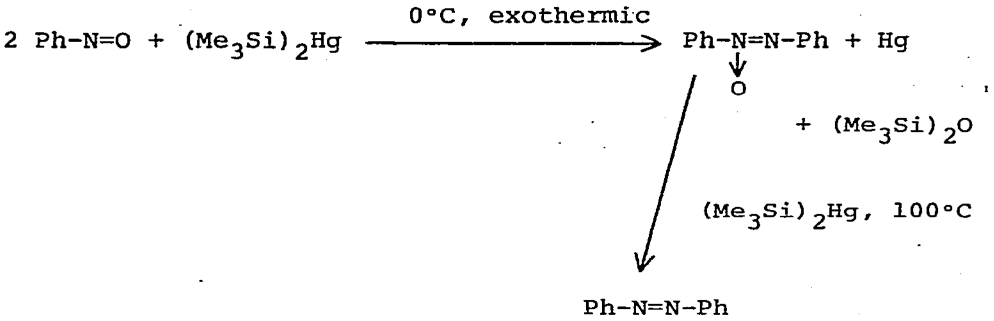
$$Ar\text{-}N{=}O + (Me_3Si)_2Hg \longrightarrow Ar\dot{N}\text{-}OSiMe_3$$

The final products are azobenzenes in the case of the less hindered nitroarenes and silylated anilines in the case of hindered nitroarenes, as shown in Scheme 5. Separate experiments showed

Scheme 5



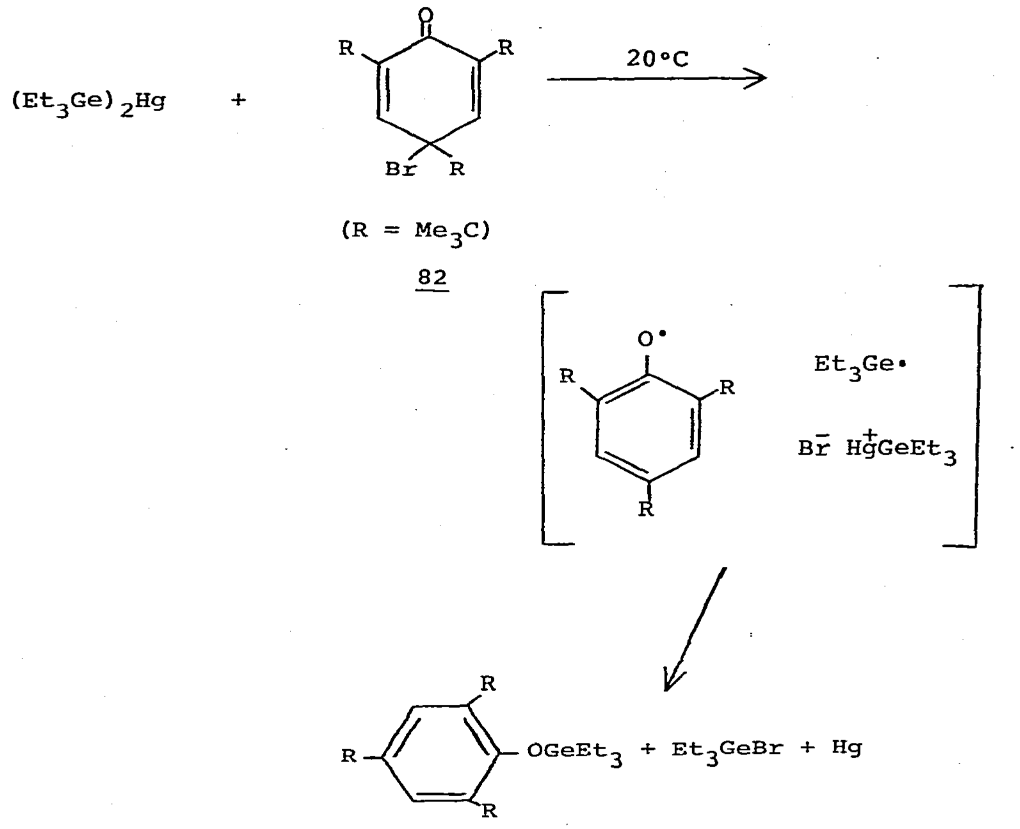
nitrosobenzene to react with $(Me_3Si)_2Hg$ in this way:



$$2\ Ph{-}N{=}O + (Me_3Si)_2Hg \xrightarrow{0°C,\ exothermic} Ph{-}\underset{\downarrow O}{N}{=}N{-}Ph + Hg + (Me_3Si)_2O$$

$$Ph{-}\underset{\downarrow O}{N}{=}N{-}Ph \xrightarrow{(Me_3Si)_2Hg,\ 100°C} Ph{-}N{=}N{-}Ph$$

Bis(triethylgermyl)mercury reacts with substituted o-quinones and 4-bromo-2,4,6-tri-tert-butylcyclohexadiene-2,5-one to give initial radical products (133):



(R = Me_3C)

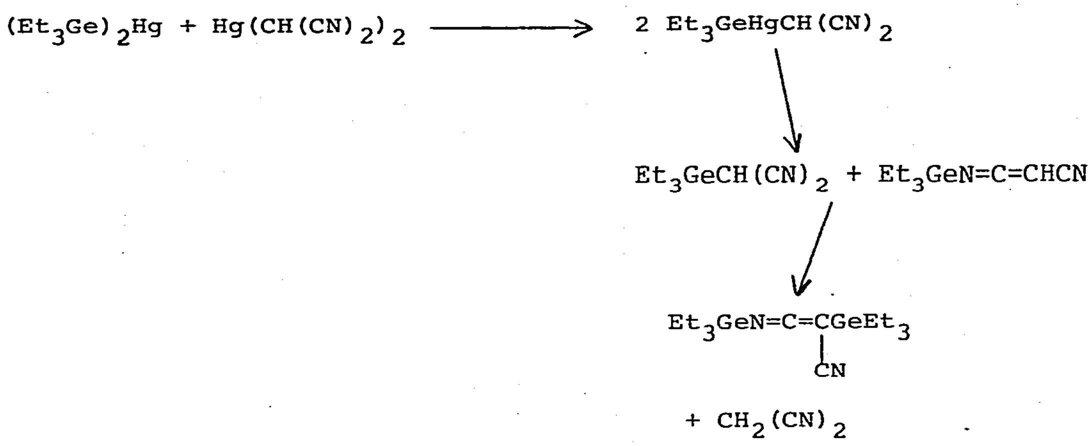
82

$(i\text{-}Pr_3Ge)_2Hg$ reacted with 82 in this manner only partially at 20°C and required a temperature of 100°C for complete reaction.

Bis(triethylgermyl)mercury reacts with α-mercurated nitriles to give α-triethylgermylnitriles (134):

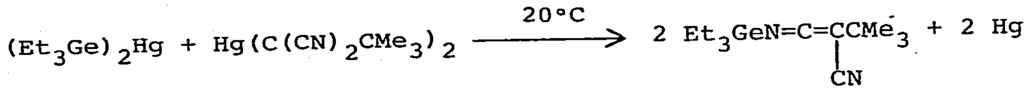
$$\begin{tikzcd}(Et_3Ge)_2Hg + Hg(CMe_2CN)_2 \arrow[r, "20^\circ C"] & 2\ Et_3GeHgCMe_2CN \arrow[d] \\ & 2\ Hg + 2\ Et_3GeCMe_2CN\end{tikzcd}$$

On the other hand, a similar reaction with mercury bis(perfluoroisobutyronitrile) in THF or toluene at 20°C gave a germanium-free nitrile, $CF_2{=}C(CF_3)CN$, and triethylfluorogermane. Bis(triethylsilyl)mercury reacts similarly. Also studied was the analogous reaction of mercury bis(malononitrile):



$$(Et_3Ge)_2Hg + Hg(CH(CN)_2)_2 \longrightarrow 2\ Et_3GeHgCH(CN)_2 \longrightarrow Et_3GeCH(CN)_2 + Et_3GeN{=}C{=}CHCN \longrightarrow Et_3GeN{=}C{=}\underset{\textstyle CN}{\underset{|}{C}}GeEt_3 + CH_2(CN)_2$$

With a substituted malononitrile the monogermylated product is stable (135):

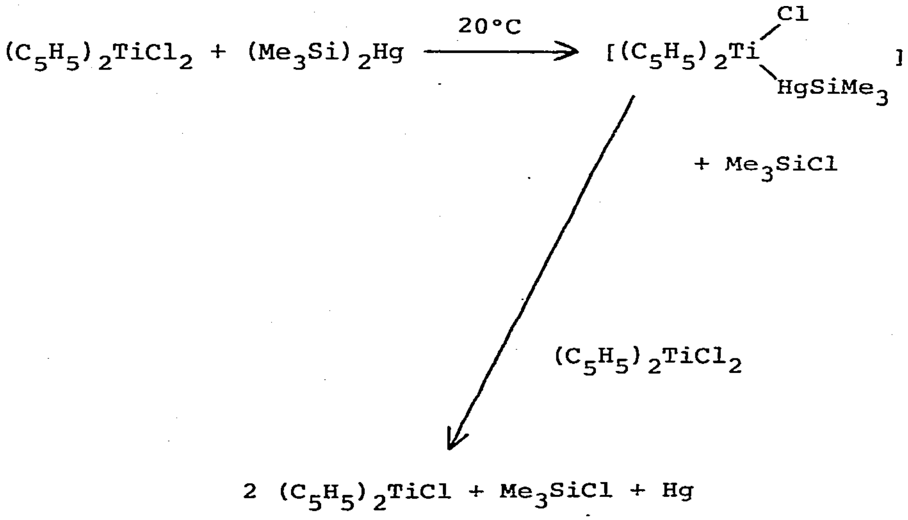


$$(Et_3Ge)_2Hg + Hg(C(CN)_2CMe_3)_2 \xrightarrow{20°C} 2\ Et_3GeN{=}C{=}\underset{\textstyle CN}{\underset{|}{C}}CMe_3 + 2\ Hg$$

The same reaction was observed with $(Et_3Si)_2Hg$.

Bis(trimethylgermyl)mercury reacts with aluminum powder in pentane/THF to give $(Me_3Ge)_3Al$ as its mono-THF adduct in 80% yield (136). An attempt to prepare $(Me_3Sn)_3Al$ by the analogous $(Me_3Sn)_2Hg/Al$ reaction at -20°C failed, apparently because the stannylaluminum compound is very unstable.

The reaction of titanocene dichloride with bis(trimethylsilyl)mercury resulted in reduction of the titanium(IV) complex (137):



$$(C_5H_5)_2TiCl_2 + (Me_3Si)_2Hg \xrightarrow{20°C} [(C_5H_5)_2Ti(Cl)(HgSiMe_3)] + Me_3SiCl$$

$$[(C_5H_5)_2Ti(Cl)(HgSiMe_3)] \xrightarrow{(C_5H_5)_2TiCl_2} 2\ (C_5H_5)_2TiCl + Me_3SiCl + Hg$$

A new preparation of $[(C_6F_5)_3Ge]_2Hg$ has been recorded (138):

$$3\ [(C_6F_5)_3Ge]_2BiEt + 3\ Hg \longrightarrow 3\ [(C_6F_5)_3Ge]_2Hg + 2\ Bi + Et_3Bi$$

8. COMPLEXES OF ORGANOMERCURIALS

n-Butylmercuric nitrate in benzene solution forms 1:1 adducts of type $n\text{-}C_4H_9HgL(ONO_2)$ with pyridine, 4-methylpyridine, 2,2'-bipyridine, triethylamine, tri-n-butylamine, tri-n-butylphosphine, triphenylphosphine and diphos (139). The stabilities and the enthalpies of formation were determined. A 4-coordinate adduct was formed with tetramethylethylenediamine. On the other hand, in water, acetone and acetonitrile, these ligands form complexes of type $n\text{-}C_4H_9HgL^+\ NO_2^-$. Also studied was the distribution of $n\text{-}C_4H_9HgNO_3$ between benzene and water as a function of added ligand. Similar calorimetric studies of adduct formation were carried out with $Hg(CN)_2$ (140). The enthalpies of adduct formation with Lewis bases and also adduct stabilities increase for selected mercurials in the order:

$$RHgX \ll Hg(C_6F_5)_2 < Hg(CN)_2 < Hg(CCl_3)_2 < Hg(SCN)_2 < HgX_2,$$

i.e., with increasing electronegativity of the substituents on mercury.

Other workers have studied the 1:1 adducts of mercuric cyanide, chloride and bromide with nicotinamide, N-methylnicotinamide and nicotinic acid (141). The solvation of $Hg(CN)_2$, $Hg(SCN)_2$ and $Hg(NO_3)_2$ in liquid ammonia has been investigated by means of Raman spectroscopy (142). Similar studies were carried out by the same group with EtHgCl, MeHgBr, MeHgI and HgX_2 (X = Cl, Br, I) (143). The following processes were found to occur in the case of the organomercuric halides:

$$RHgX + 3\ NH_3 \xrightarrow{\text{liq. } NH_3} RHg(NH_3)_3^+ + X^-$$

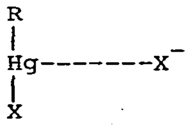
(RHgX = MeHgBr, EtHgCl)

$$\begin{tikzcd} MeHgI + 2\ NH_3 \arrow[r, "\text{liq. } NH_3"] & MeHgI(NH_3)_2 \arrow[d] \\ & {[MeHg(NH_3)_3]^+\ [I(solvated)]^-} \end{tikzcd}$$

The formation of alkylmercuric halide complex anions was examined using vibrational and NMR spectroscopy. Complex anions of type $[RHgX_2]^-$ were found to be formed with RHgCl (R = Me, Et, n-Pr, n-Bu), RHgBr (R = Me, Et, n-Pr, n-Bu), RHgI (R = Me, Et) and MeHgSCN in benzene, chloroform, dichloromethane, THF and acetonitrile, but not in methanol and water (144):

$$RHgX + \underline{n}\text{-}Bu_4N^+X^- \longrightarrow [\underline{n}\text{-}Bu_4N^+] \quad [RHgX_2^-]$$

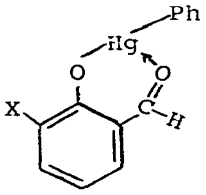
Attempts to isolate such complexes failed. A monomeric structure in which essentially linear R-Hg-X molecules weakly bond the added ligand, 83, was suggested.



$$\begin{array}{l} R \\ | \\ Hg\text{-------}X^- \\ | \\ X \end{array}$$

83

Infrared evidence has been presented for intramolecular coordination between mercury and the C=O group in mercurated ortho-formylphenols (145):

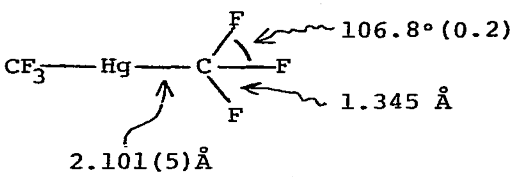


(X = halogen, CH=O)

Electronic emission spectroscopy at 77°K has been used to obtain evidence for the formation of contact complexes between diarylmercurials and dioxygen (146). In these complexes it appears that the mercurial is the acceptor, the O_2 molecule the donor. Other workers have found electron transfer from aromatic molecules to dimethylmercury to occur via a triplet exciplex involving an electronically excited aromatic species and two molecules of dimethylmercury (147).

9. STRUCTURAL STUDIES OF ORGANOMERCURIALS AND RELATED COMPOUNDS

The gas phase molecular structure of $(CF_3)_2Hg$ has been determined by means of electron diffraction (148):



X-ray diffraction was used in the structural investigation of $CF_3HgN{=}C{=}O$ (Fig. 2) and CF_3HgN_3 (Fig. 3) (149). Both exist as nitrogen-bridged dimers.

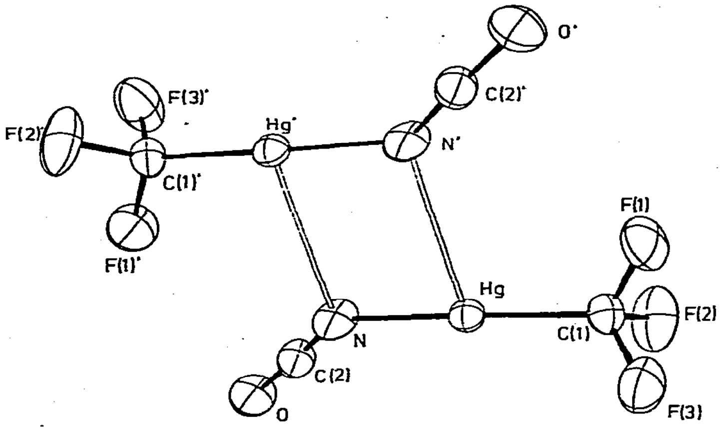
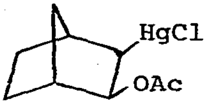


Figure 2. Structure of Dimeric CF_3HgNCO. From D.J. Brauer, H. Bürger, G. Pawelke, K.H. Flegler and A. Haas, J. Organometal. Chem., 160 (1978) 389.

Grdenić has reported the structure of $C(HgCN)_4 \cdot H_2O$, as determined by X-ray diffraction (Fig. 4) (150). This compound was prepared by the action of potassium cyanide on $C(HgOAc)_4$. Also investigated have been the structures of the oxymercuration products of norbornene, 84 (Fig. 5) (151) and aldrin, 85 (Fig. 6) (152). Both of these compounds come from the oxymercuration of strained olefins, so *cis*, rather than *trans*, addition has occurred.



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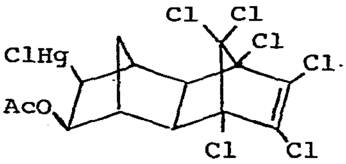

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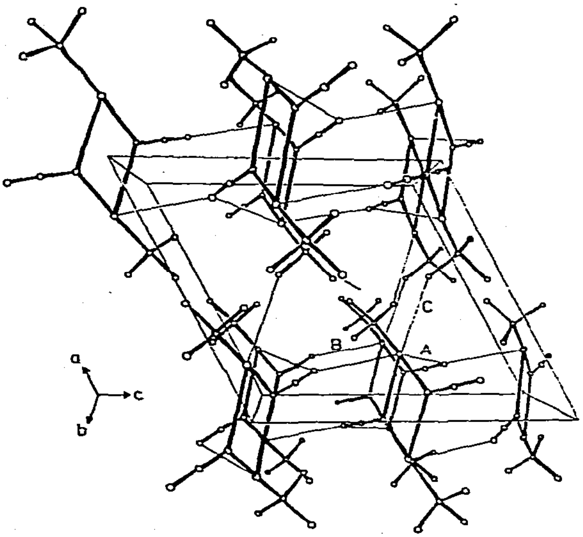


Figure 3. Unit Cell of Dimeric α-CF_3HgN_3. From D.J. Brauer, H. Bürger, G. Pawelke, K.H. Flegler and A. Haas, J. Organometal. Chem., 160 (1978) 389.

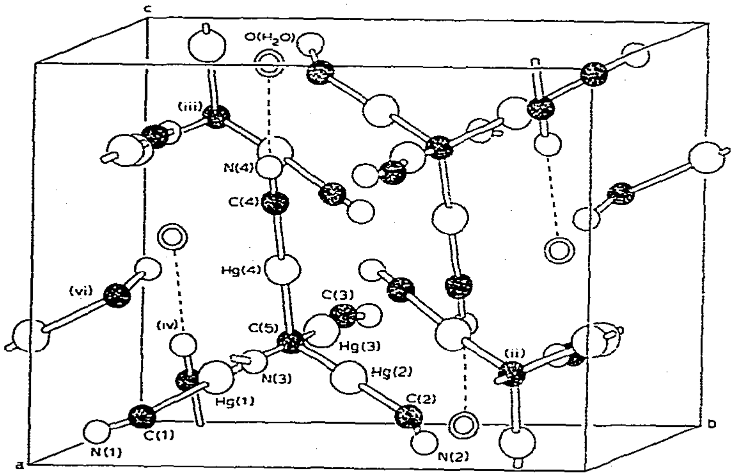


Figure 4. The Unit Cell of Tetrakis(cyanomercuri)methane. From D. Grdenić, M. Sikirica and B. Korpar-Colig, J. Organometal. Chem., 153 (1978) 1.

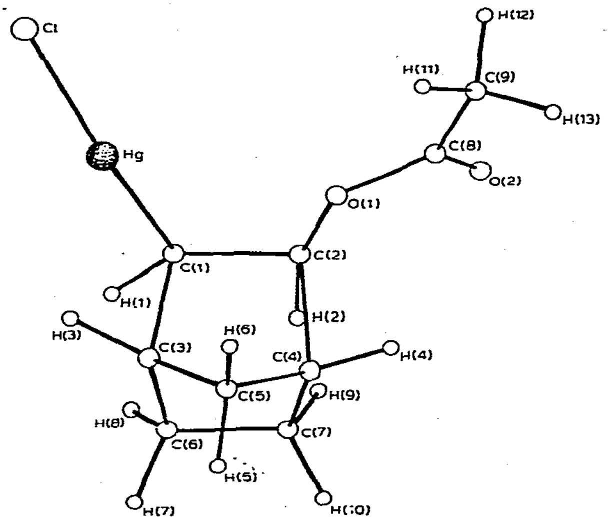


Figure 5. Molecular Structure of 2-exo-(Chloromercuri)-3-exo-acetoxybicyclo[2.2.1]heptane. From J. Halfpenny, R.W.H. Small and F.G. Thorpe, Acta Cryst. B 34 (1978) 3077.

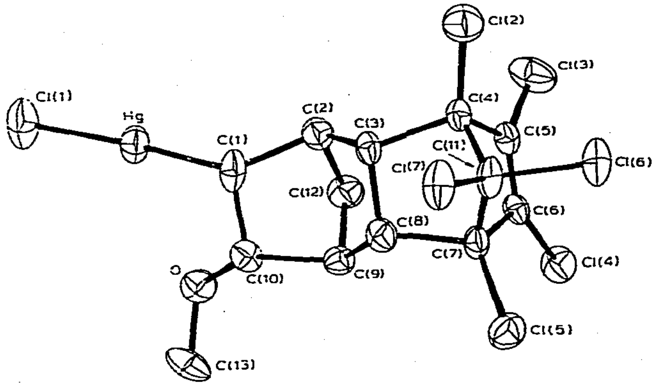


Figure 6. Molecular Structure of exo-6-Chlormercuri-6,7-dihydro-exo-7-methoxyaldrin. From J.L. Atwood, L.G. Canada, A.N.K. Lau, A.G. Ludwick and L.M. Ludwick, J. Chem. Soc. Dalton Trans. (1978) 1573.

The o-phenylenemercury prepared by reaction of 1,2-dibromobenzene with sodium amalgam in diethyl ether was shown by X-ray crystallography to be the trimer, tribenzo[b,e,h][1.4.7]trimercuronin, Fig. 7. (153).

A crystal structure of some interest is that of trans -di-μ-iodobis(triphenylphosphonium cyclopentadienylide)dimercury since solution spectroscopic studies did not unequivocally distinguish between possible σ or π coordination of the C_5 ligand to mercury. In the solid state, the dimeric molecule is of the η^1 type, as shown in Fig. 8 (154), with iodine bridges. In this

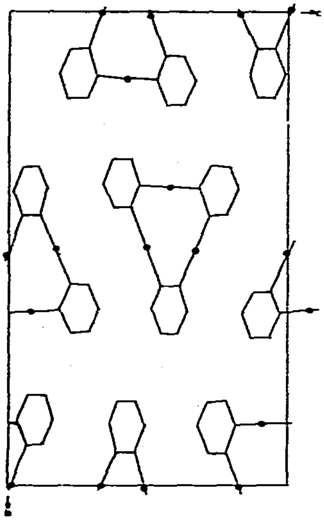


Figure 7. Structure of Tribenzo[b,e,h][1,4,7]trimercuronin. Unit cell contents projected down a. From D.S. Brown, A.G. Massey and D.A. Wickens, Acta. Cryst. B 34 (1978) 1695.

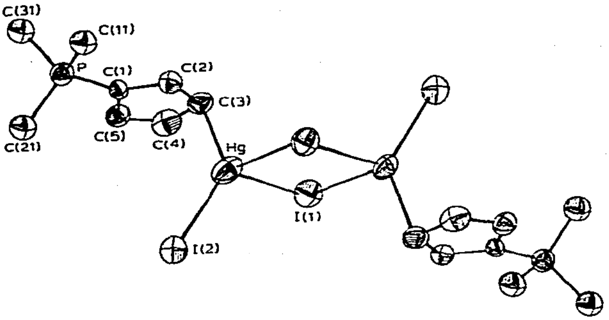


Figure 8. An ORTEP Plot of trans-Di-μ-iodobis(triphenylphosphonium cyclopentadienylide)dimercury. Only the C atoms attached to P are shown for the phenyl groups. From N.C. Baenziger, R.M. Flynn, D.C. Swenson and N.L. Holy, Acta Cryst. B 34 (1978) 2300.

molecule d(C-Hg) = 2.292(8) Å. Also of interest is the crystal structure of 1-methylmercuri-2-chloromethyl-o-carborane (Fig.9) (155). NMR studies had suggested that there is an intramolecular donor/acceptor interaction between Cl and Hg in solution (Federov et al., 1970, 1971). In the solid state, the Cl····Hg distance is 3.27(3) Å, just about equal to the sum of the van der Waals radii of Cl and Hg (3.3 Å). This does not exclude a weak intramolecular Cl⟶Hg coordination, and the C-Hg-Cl angles (see Fig. 9) speak in favor of such bonding.

The solid state structures of several methylmercury(II) derivatives have been determined.

$[CH_3Hg(NC_5H_5)]^+ NO_3^-$ (Fig.10) (156), which is composed of $[CH_3Hg(py)]^+$ cations with a linear C-Hg-N moiety and uncoordinated nitrate anions.

$[CH_3Hg(3,3'-Me_2-2,2'-bipy)]^+ NO_3^-$ (Fig.11) (157). The cation has a bent C(1)-Hg-N(1) moiety. Weak interaction between Hg and the oxygen atoms of NO_3 and between Hg and the second pyridyl ring of the bipy ligand appears to be taking place.

Methyl(2-mercaptopyrimidinato)mercury(II), 86, in which there is a strong interaction between mercury and one of the ring nitrogen atoms, with d(Hg-N) = 2.83 Å (Fig. 12) (158).

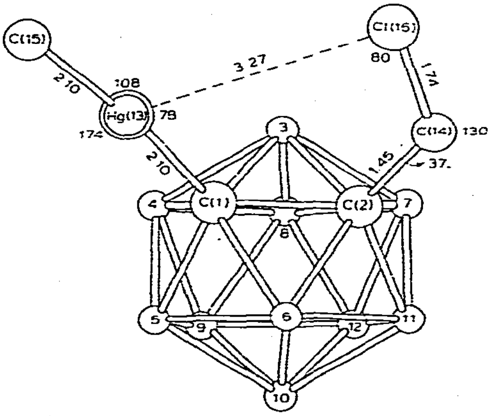


Figure 9. Structure of 1-Methylmercuri-2-chloromethyl-o-carborane. From N.G. Bokii, Yu. T. Struchkov, V.N. Kalinin and L.I. Zakharkin, Zh. Strukt. Khim., 19 (1978) 380.

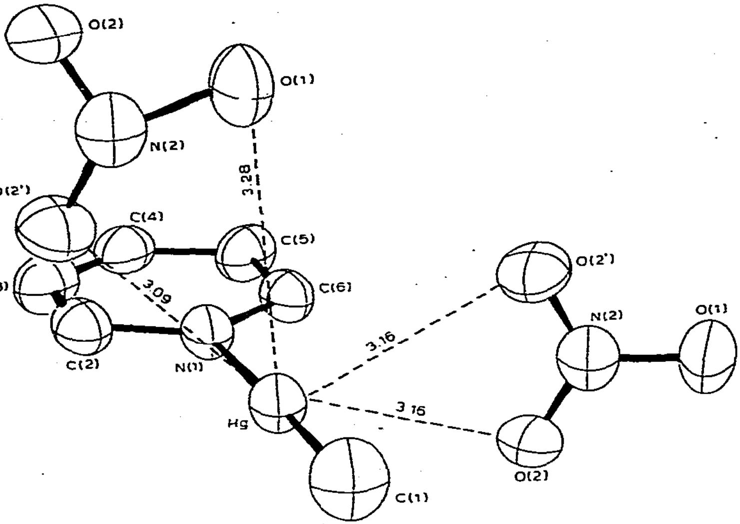


Figure 10. Structure of Methyl(pyridine)mercury(II) Nitrate. Perspective view of the compound with thermal ellipsoids scaled to 50% probability. From R.T.C. Brownlee, A.J. Canty and M.F. Mackay, Austral. J. Chem., 31 (1978) 1933.

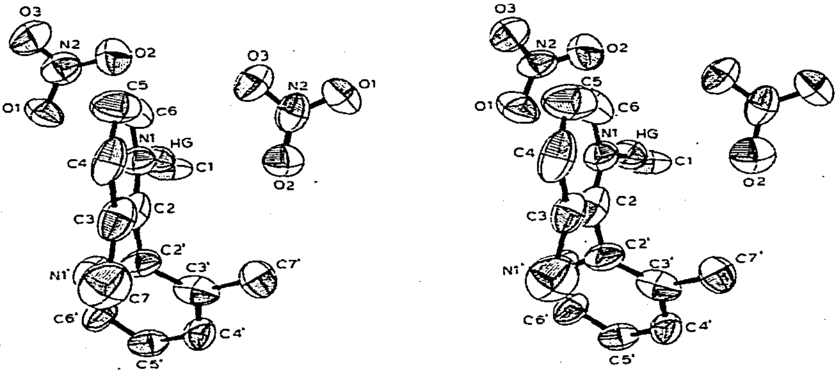


Figure 11. Stereoscopic View of the Structure of Methyl(3,3'-dimethyl-2,2'-bipyridyl)mercury(II) Nitrate. The relationship between Hg and the nearest nitrate ion is shown. From A.J. Canty, N. Chaichit, B.M. Gatehouse and A. Marker, Acta Cryst. B 34 (1978) 3229.

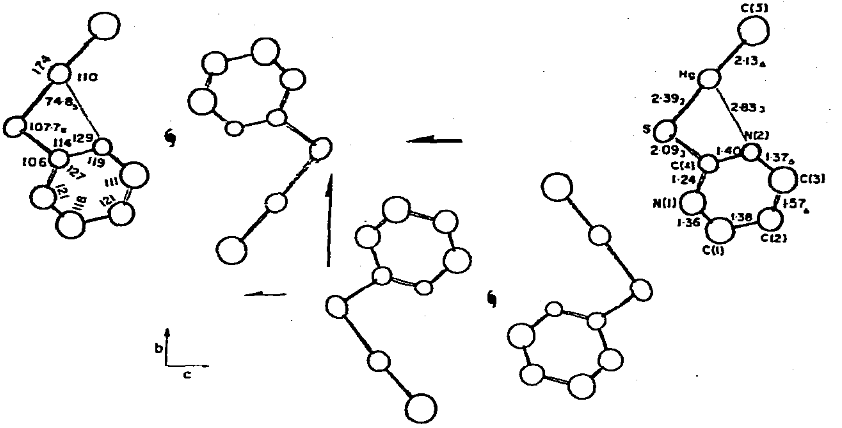
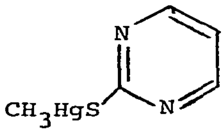
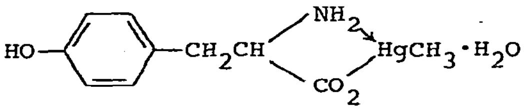


Figure 12. Packing Diagram for Methyl(2-mercaptopyrimidanato)-mercury (II). From C. Chieh, Can. J. Chem., 56 (1978) 560.



86

Methyl(L-tyrosinato)mercury(II) monohydrate, 87 (Fig.13), and methyl(L-)2-amino-4-phenylbutanato)mercury(II), 88 (Fig.14) (159).



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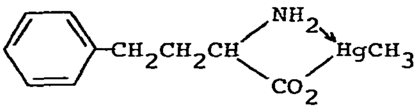


88

In 87, Hg is coordinated to tyrosine through the amino group; there are further interactions with a CO_2^- oxygen and the phenyl ring. In 88, on the other hand, there is no Hg-aromatic interaction and there is both intra- as well as intermolecular Hg-O bonding. The principal binding of the ligand to mercury is through the amino group.

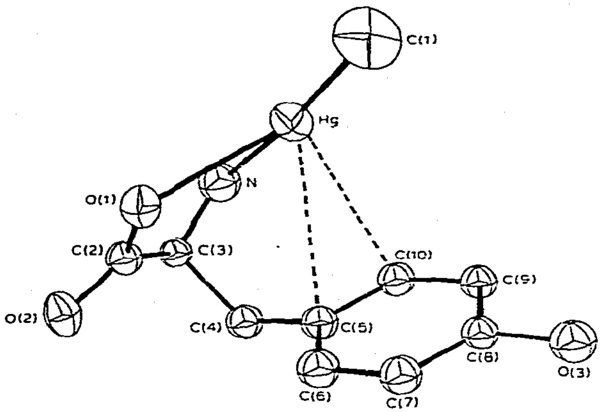


Figure 13. Molecular Structure of Methyl(L-tyrosinato)-mercury(II). From N.W. Alcock, P.A. Lampe and P. Moore, J. Chem. Soc. Dalton Trans. (1978) 1324.

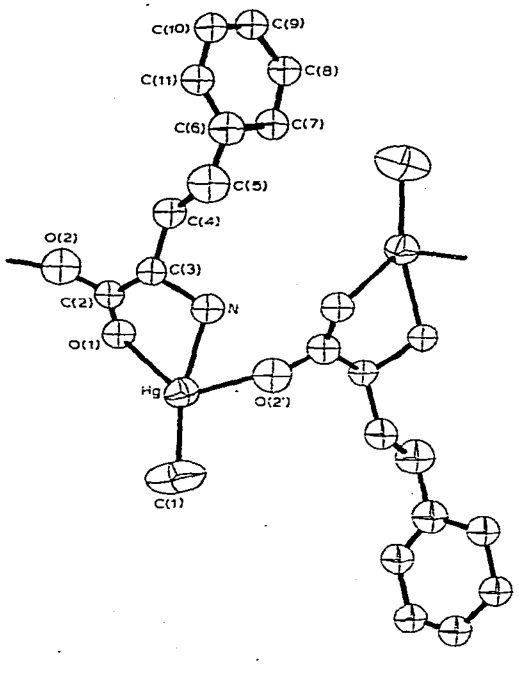
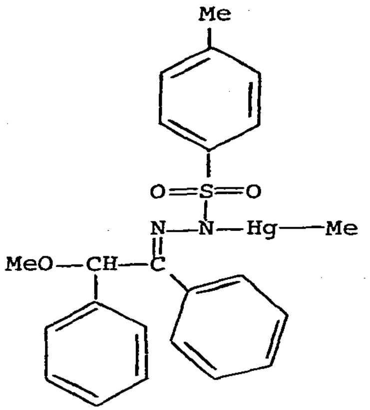


Figure 14. Molecular Structure of Methyl(L-(2-amino-4-phenylbutanato)mercury(II). From N.W. Alcock, P.A. Lampe and P. Moore, J. Chem. Soc. Dalton Trans. (1978) 1324.

o-Methylbenzoin methylmercurio(p-tolylsulfonyl)hydrazone, 89 (Fig.15) (160).



89

A linear C-Hg-N configuration is present. The Hg-O distances (SO_2 oxygens) of 2.89 and 2.93 Å indicate the occurence of significant Hg·····O interaction.

The structures of some phenylmercury(II) derivatives also have been determined.

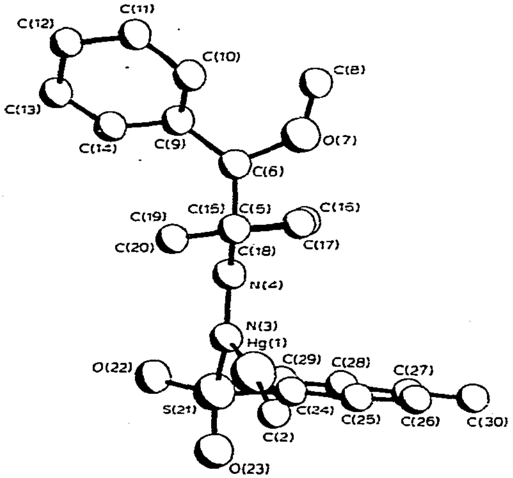


Figure 15. Molecular Structure of o-Methylbenzoin methylmercuri(p-tolylsulfonyl)hydrazone. From A. Medici, G. Rosini, E.F. Serantoni and L.R. di Sanseverino, J. Chem. Soc. Perkin Trans. I (1978) 1110.

PhHgCN·o-phenanthroline (Fig. 16) (161). The mercury atom is four-coordinate. The C-Hg-CN angle (177) is very similar to that in PhHgCN (176°). The individual molecules are held together only by van der Waals forces.

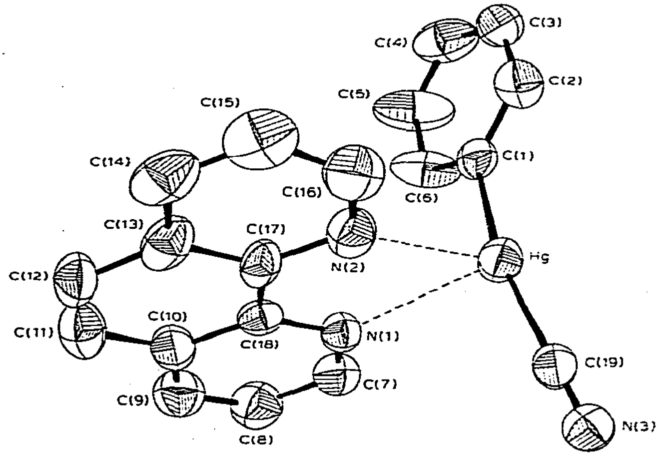
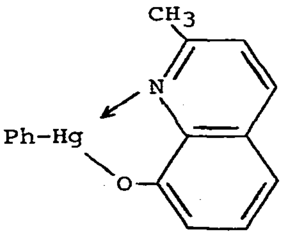


Figure 16. Molecular Structure of Phenylmercuric Cyanide-o-phenanthroline. From A. Ruiz-Amil, S. Martinez-Carrera and S. Garcia-Blanco, Acta Cryst. B 34 (1978) 2711.

Phenylmercury(II) quinaldinate, 90, and two phases of phenylmercury(II) oxinate, 90 (162). In 90, dimeric units are present (Fig. 17 and 18). The two phases of 91 differ in how the molecules are disposed in the crystal (Fig. 19 and 20).



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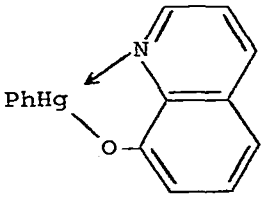


91

$[Mg_4(OCH_2CH_2OCH_3)_6(CH_3OCH_2CH_2OCH_3)_2{}^{+2}]\ [Hg(Si(CH_3)_2C_6H_5)_3{}^{-}]_2$.

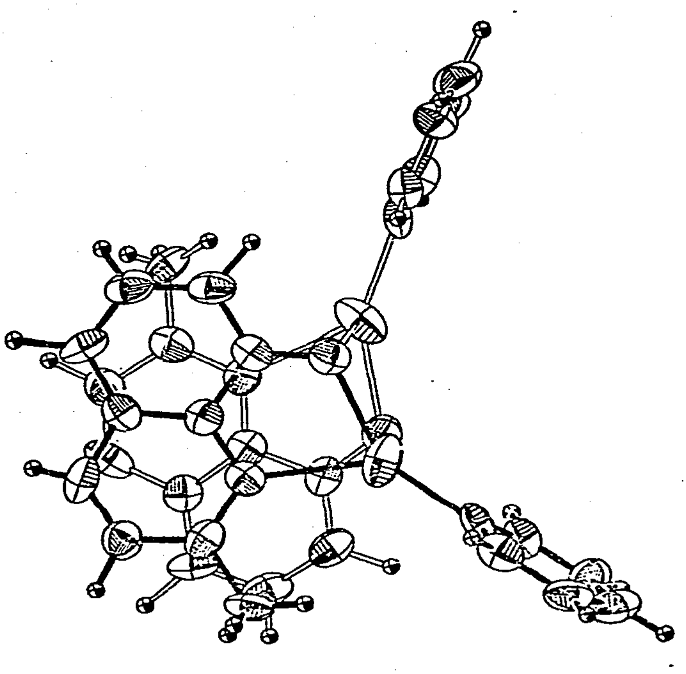


Figure 17. Molecular Structure of the Phenylmercury(II) Quinaldinate Dimer. View projected normal to the plane of the ligand nearest the viewer (black bonds), showing 50% thermal ellipsoids and displaying the relative disposition of the two molecules. From C.L. Raston, B.W. Skelton and A.H. White, Austral. J. Chem., 31 (1978) 537.

This complex anion which contains three Hg-Si bonds shows trigonal planar symmetry around the mercury atom, d_{ave}(Si-Hg)= 2.516 Å, average Si-Hg-Si angle = 119.8°(163). The complex was prepared by the action of metallic magnesium on $Hg(SiMe_2Ph)_2$ in 1,2-dimethoxyethane. Solvent cleavage obviously occurred during the reaction.

A few compounds of mercury which do not contain Hg-C bonds have been the subjects of structural investigations, but they may be of interest to organomercury specialists and, therefore, we mention them briefly.

$CH_3SHgO_2CCH_3$ Polymer (Fig. 21), $CH_3SHgO_2CCH_3 \cdot NC_5H_5$ (Fig. 22) and $(Me_3CS)_4Cl_4Hg_4(C_5H_5N)_2$ (Fig.23) (164).

(Continued on p.245)

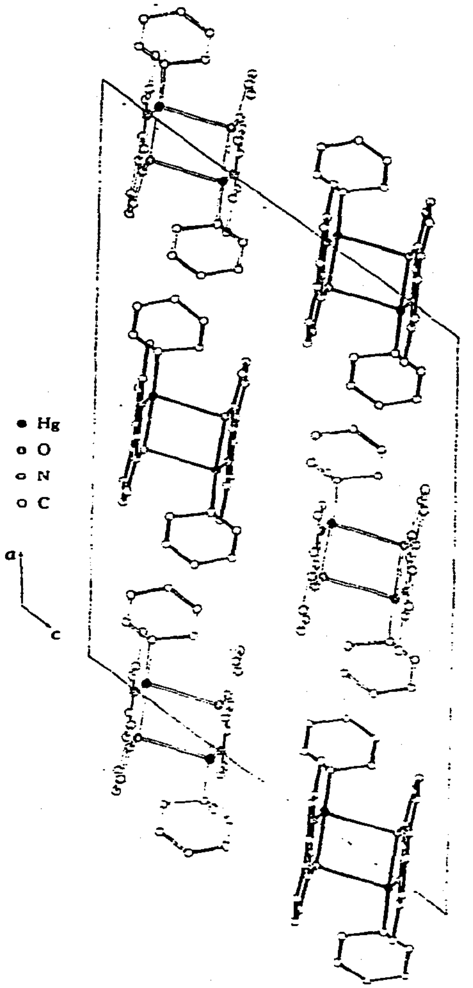


Figure 18. Crystal Structure of Phenylmercury(II) Quinaldinate. Unit cell contents, projected along b. From C.L. Raston, B.W. Skelton and A.H. White, Austral. J. Chem., 31 (1978) 537.

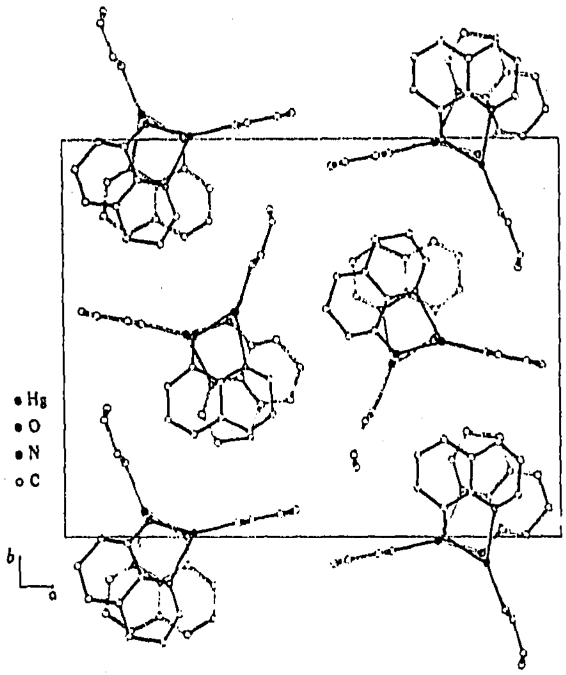


Figure 19.

Crystal Structure of Phenylmercury(II) Oxinate. Unit cell contents of one phase, projected along c. From C.L. Raston, B.W. Skelton and A.H. White, Austral. J. Chem., 31 (1978) 537.

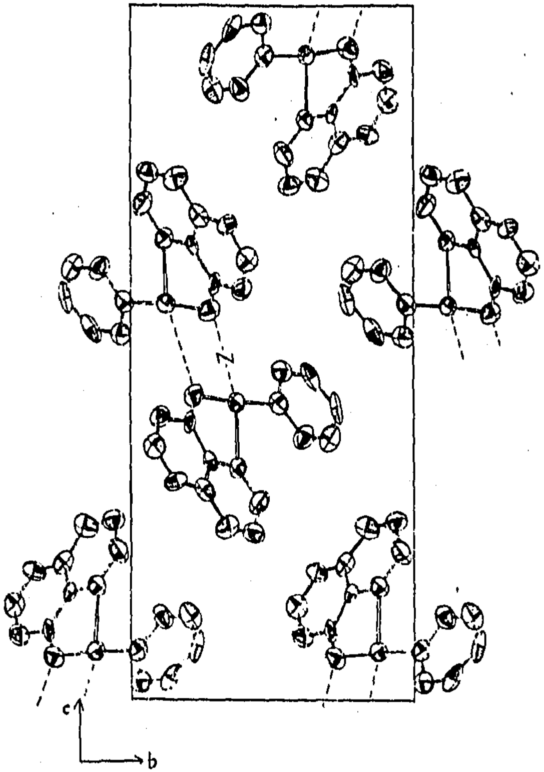
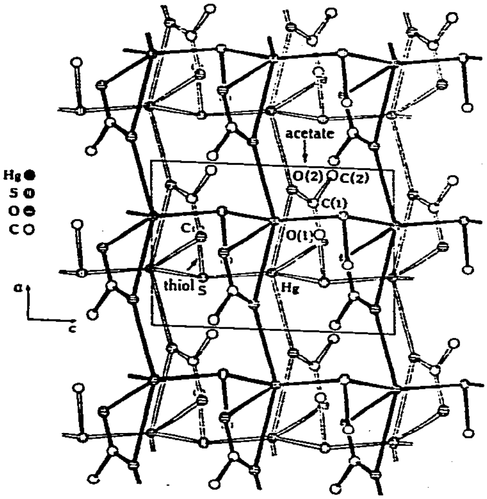


Figure 20.

Crystal Structure of Phenylmercury(II) Oxinate. Unit Cell contents of the other phase, projected along a. Intermolecular Hg-O contacts are shown by broken lines. From C.H. Raston, B.W. Skelton and A.H. White, Austral. J. Chem., 31 (1978) 537.



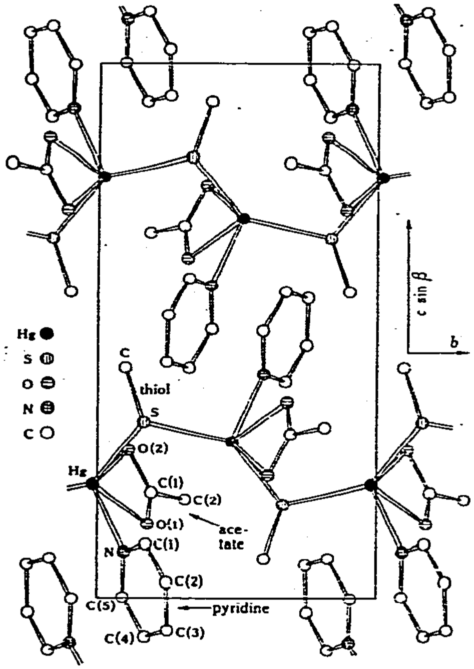


Figure 21. Structure of $CH_3SHgO_2CCH_3$ Polymer, projected along b. From A.J. Canty, C.L. Raston and A.H. White, Austral. J. Chem., 31 (1978) 677.

Figure 22. Crystal Structure of $CH_3SHgO_2CCH_3$ Monopyridinate. Unit cell contents, projected along a. From A.J. Canty, C.L. Raston and A.H. White, Austral. J. Chem., 31 (1978) 677.

$(CF_3CO_2)_2Hg(C_5H_5N)_2$ (Fig.24) (165) and $(CF_3CO_2)_2Hg(C_5H_5N)_3$ (Fig. 25) (166).

10. SPECTROSCOPIC STUDIES OF ORGANOMERCURIALS

A. Vibrational Spectroscopy

The IR and Raman spectra in solution (THF, CH_2Cl_2, $CDCl_3$ and C_6H_6) of CF_3HgX (X = Cl, Br, I, CF_3) and CCl_3HgX (X = Cl, Br, CCl_3) and of the solids have been studied. Complete assignments of vibrational fundamentals were made (167). In solution these compounds appear to be monomeric. Also investigated were the vibrational spectra of CF_3HgN_3 and CF_3HgNCO (149). Goggin and Hurst (168) have presented the results of a detailed study of IR and Raman intensities of stretching vibrations in HgX_2 (X = Cl, Br, I), CH_3HgX (Cl, Br, I) and $(CH_3)_2Hg$ in solution

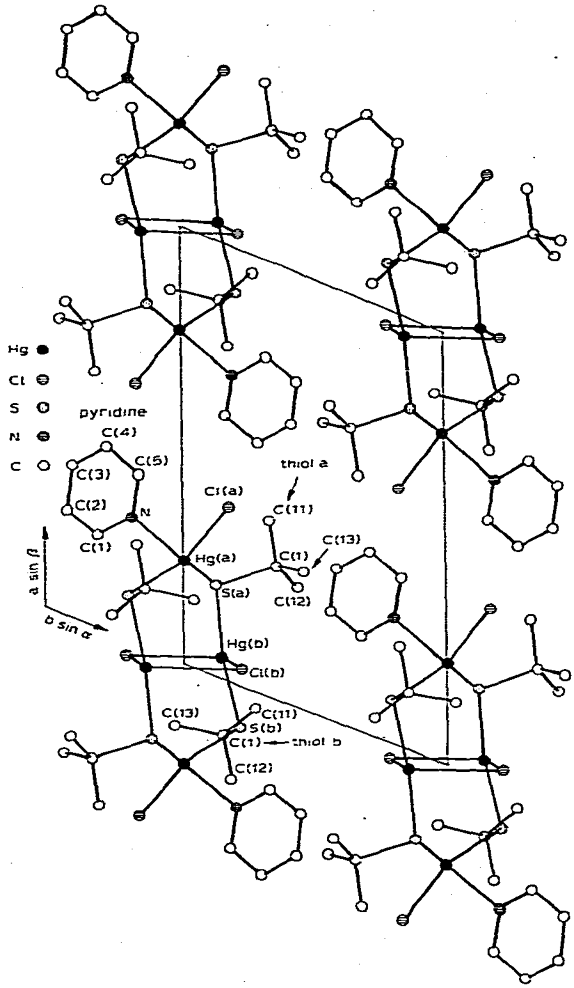


Figure 23. Crystal Structure of $(Me_3CS)_4Cl_4Hg_4(C_5H_5N)_2$. Unit cell contents projected along c. From A.J. Canty, C.L. Raston and A.H. White, Austral. J. Chem., 31 (1978) 677.

and used them to estimate the charge distribution in CH_3HgX and HgX_2. Mink and Goggin (169) have calculated force constants of methylmercury compounds, CH_3HgY (Y = CH_3, Cl, Br, I, SCH_3, CN and $AsMe_3^+$). Other workers have investigated solvation of HgX_2 and RHgX (X = Cl, Br, I) in liquid ammonia solution using Raman spectroscopy (143). A single crystal IR study of $HgCl_2$ and $HgBr_2$ has been reported (170).

IR and Raman spectra of C_6H_5HgY and C_6D_5HgY compounds (Y = $C_6H_5(C_6D_5)$, Cl, Br, I, CN, OAc) have been studied in detail (171).

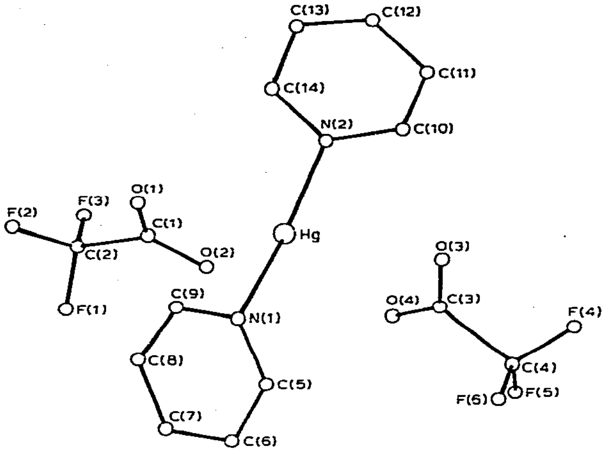


Figure 24. Perspective View of the Asymmetric Unit of Bis (pyridine)mercury(II) Bis(trifluoroacetate). From J. Halfpenny, R.W.H. Small and F.G. Thorpe, Acta Cryst. B 34 (1978) 3075.

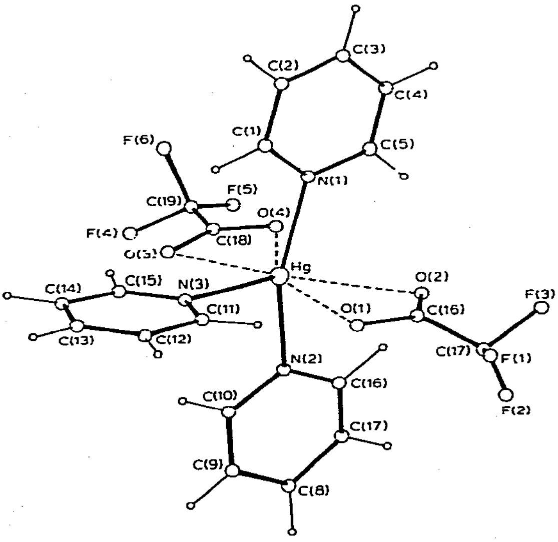


Figure 25. A Unit of the Structure of Tris(pyridine)mercury (II) Bis(trifluoroacetate) Showing the Coordination Around Mercury. From J. Halfpenny and R.W.H. Small, Acta. Cryst. B 34 (1978) 3758.

Mercury- chlorine stretching frequencies of some polyfluoroarylmercuric chlorides have been reported (86).

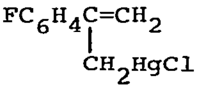
The aromatic ring and nitro group stretching vibrations in $O_2NC_6H_4SMR_n$ (172) and $O_2NC_6H_4OMR_n$ (173), including R_nM = PhHg, $SnPh_3$, $PbPh_3$ and $SbPh_4$, have been shown to be useful probes of the electron-donating capacity of the organometallic groups, R_nM.

The IR spectra of mercurated carboranes have been investigated by two Russian groups (127, 174).

B. Nuclear Magnetic Resonance Spectroscopy

The following NMR studies have been reported.

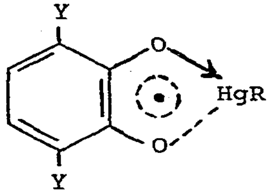
- ^{1}H, ^{13}C, ^{199}Hg NMR spectroscopy of dimethylmercury, in connection with the relativistic theory of nuclear spin-spin coupling in molecules (175)
- ^{13}C and ^{199}Hg NMR spectra of diverse RHgX (41). Results are given in Table 16.
- ^{199}Hg NMR study of $CH_3Hg(II)$ and Hg(II) in aqueous solution (176)
- ^{199}Hg NMR study of 2- (L = py) and 3- (L = 2,2'-bipy) coordinate $[CH_3HgL]^+NO_3^-$ compounds (177). The ^{199}Hg chemical shifts in the complexes are downfield from $MeHgNO_3$, not upfield as stated in the paper: A.J. Canty, private communication.
- ^{1}H and ^{199}Hg NMR spectra of methyl-substituted benzylmercuric chlorides (178). Here ^{199}Hg shielding constants were used to obtain information on σ-π conjugation in these molecules.
- ^{13}C, ^{29}Si and ^{199}Hg NMR spectroscopy of diverse silyl and germyl mercury compounds (128).
- ^{19}F NMR studies of fluorophenyl-substituted mercurials (179):

$FC_6H_4CH{=}CHCH_2HgCl$, 
$FC_6H_4C(CH_2HgCl){=}CH_2$, FC_6H_4HgCl

- ^{11}B-{^{1}H} NMR spectra of C-mercurated carboranes (174).

C. Electron Spin Resonance Spectroscopy

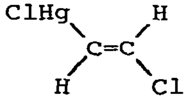
ESR studies have served to characterize radical intermediates in the reactions of dialkylmercurials with sterically hindered *o*-quinones. ESR parameters were given for 92 (R = Me, Et, *n*-Pr, *n*-Bu, cyclo-C_6H_{11}, t-Bu and Y = H and t-Bu) (180).

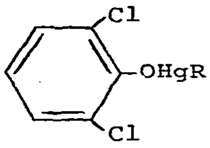


92

D. Nuclear Quadrupole Resonance Spectroscopy

A variable-temperature, variable-pressure NQR study of diverse polychlorinated mercurials has been reported (181). Among the compounds examined were the following:

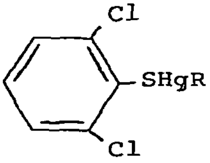




(R = Ph, $PhCH_2$, $C_6H_4NMe_2$).

CCl_3HgR

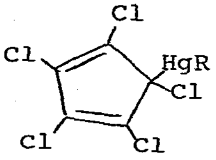
(R = CCl_3, Ph, Cl, Br)



(R = Ph)

$RHgC_6Cl_5$

(R = C_6Cl_5, Cl, Br, CH_3)



(R = C_5Cl_5, Cl, Ph, Cl, Br)

E. Photoelectron Spectroscopy

A new hollow cathode lamp has permitted the measurement of the Hg $5d_{5/2}$ spectrum of dimethylmercury with better resolution (182). Additional peaks not previously seen were identified. As a result, the Hg 5d orbital energy-ordering for $(CH_3)_2Hg$ was reassigned: $\pi > \delta > \sigma$. This new ordering retains the implication that the Hg $5d_z2$ orbital is involved in bonding.

Cradock and Duncan (183) have studied the photoelectron spectrum of dicyclopentadienylmercury (prepared by reaction of C_5H_5Tl with mercuric chloride in THF at -40°C). An interpretation in terms of a peripherally-bonded structure was given.

(Continued on p.252)

TABLE 16. ^{13}C and ^{199}Hg NMR Parameters of Some RHgX (41)

Compound	Cα		Cβ		Cγ		Cδ		
	δ	$^1J(HgC)$	δ	$^2J(HgC)$	δ	$^3J(HgC)$	δ	$^4J(HgC)$	$\delta(^{199}Hg)$
$HgMe_2$	23.5	692[b]							-11[c]
$HgEt_2$	36.1	647	13.4	24					-307[d,e]
$HgPr^i_2$	49.2	636	23.4	27					-600[d,e]
$HgBu^t_2$	59.4	637	31.3	28					-838
$HgPr^n_2$	47.2	660	22.3	26	19.9	102			-213[d,e]
$HgBu^n_2$	44.2	659	31.1	27	28.4	100	14.0	ca.0	-208[d,e]
$HgPh_2$	170.4	1 176	137.5	85	128.5	101	128.2	18	-745[d,f]
[HgCl(Me)]	8.6	1 431[b]							-813
[HgCl(Et)]	25.1	1 474	13.9	92					-978
$[HgCl(Pr^i)]$	43.1	1 555	24.0	62					-1 128
$[HgCl(Bu^t)]$	57.9	1 619	32.4	17					-1 245
$[HgCl(Pr^n)]$	35.8	1 469	22.2	87	19.1	187			-947
$[HgCl(Bu^n)]$	33.2	1 444	30.6	86	27.9	177	13.5	ca.0	-944
[HgCl(Ph)]	150.5[g]	2 530	136.4	117	128.0	205	127.9	35	-1 192[h]
[HgBr(Me)]	12.8	1 394[b]							-915[i]
[HgBr(Et)]	28.8	1 414	13.9	89					-1 070
$[HgBr(Pr^i)]$	46.6	1 528	24.2	64					-1 202
$[HgBr(Pr^n)]$	39.6	1 407	22.4	85	19.1	182			-1 039

[HgBr(Bu^n)]	36.9	1 401	30.9	82	27.8	175	13.5	ca.0	-1 036
[HgI(Me)]	18.8	1 301[b]							-1 097[i]
[HgI(Et)]	34.8		14.2						
[HgI(Bu^n)]	42.3		31.3		27.6		13.6		

---

[a] Chemical shifts in p.p.m. to high frequency of $SiMe_4$ (^{13}C) and neat $HgMe_2$ (^{199}Hg), coupling constants in Hz. Except where otherwise indicated, $^{13}C-\{^1H\}$ measurements were on $CDCl_3$ solutions and $^1H-{}^{199}Hg$ measurements on benzene solutions (≤ 0.2 mol dm^{-3}).
[b] Ref. 13. [c] M.A. Sens, N.K. Wislon, P.D. Ellis, and J.D. Odom, J. Magnetic Resonance, 1975, 19, 323; 1 mol dm^{-3} in CCl_4. [d] A.P. Tupciauskas, N.M. Sergeyev, Yu.A. Ustynyuk, and A.N. Kashin, J. Magnetic Resonance, 1972, 7, 124. [e] 2 mol dm^{-3} in CCl_4. [f] 1 mol dm^{-3} in CH_2Cl_2. [g] In dimethylformamide + $(CD_3)_2CO$ (20%) at 340 K (saturated solution). [h] In tetrahydrofuran (saturated). [i] 0.2 mol dm^{-3} in CH_2Cl_2.

11. ANALYTICAL ASPECTS OF ORGANOMERCURY CHEMISTRY

Papers on the following topics are noted:

- GLC determination of trace amounts of inorganic mercury by conversion of Hg(II) to Ph_2Hg by reaction with $NaBPh_4$ (184):

$$NaBPh_4 + 2\ HgX_2 + 3\ H_2O \longrightarrow 2\ Ph_2Hg + 3\ HCl + NaCl + B(OH)_3$$

$$(X = Cl,\ NO_3)$$

The Ph_2Hg is extracted with toluene. Nanogram quantities of Hg(II) can be determined by this method.

- Molecular activation analysis for $CH_3Hg(II)$. This procedure was not successful in attempted application to the species specific determination of methylmercury(II) in fish (185).
- Dithizone extraction of RHg(II) (R = Me, Et, Ph), i.e., the distribution of RHg(II) between aqueous phases and pure CCl_4 or solutions of dithizone in CCl_4 (186).
- The use of $CH_3{}^{203}HgCl$ in analysis (187).
- The solubility of CH_3HgCl and C_2H_5HgCl in water (188, 189).

12. MISCELLANEOUS

Miscellaneous items involving organomercurials include:

- Calculations of the stabilities of cis- and trans-ClCH=CH-HgCl (190)
- The use of $CH_3Hg(II)$ as a spin-orbit probe (effect of complexing on the excited state of tryptophan, tryptamine and benzimidazole)(191).
- The breakdown of organomercury compounds in aqueous solution (192).
- The sulfur-containing polymers which strongly bind Hg(II) and $CH_3Hg(II)$: a brief review (193).

Finally, we note the commercial availability of highly porous, water-insoluble polymeric amine-borane acrylic- and styrene-based resins which find application in the reduction of Hg(I), Hg(II) and $CH_3Hg(II)$ (194). The mercury obtained is retained in the highly porous resin and may be recovered.

13. REFERENCES

1. J.K. Kochi, "Organometallic Mechanisms and Catalysis", Academic Press, New York, 1978, xvii + 623 pages.
2. R.C. Larock, Angew. Chem., 90 (1978) 28; Angew Chem. Int. Ed. Engl., 17 (1978) 27.
3. O.A. Reutov, Pure Appl.Chem., 50 (1978) 717.
4. O.A. Reutov, Tetrahedron, 34 (1978) 2827.
5. D.L. Rabenstein, Acct. Chem. Res., 11 (1978) 100.
6. D.L. Rabenstein, J. Chem. Educ., 55 (1978) 292.
7. F.E. Brinckman and J.M. Bellama, ed., ACS Symposium Series, 82 (1978).
8. S. Al-Hashimi and J.D. Smith, J. Organometal. Chem., 153 (1978) 253.
9. D. Seyferth and S.C. Vick, J. Organometal. Chem., 144 (1978) 1.
10. A.N. Nesmeyanov, V.A. Blinova, I.V. Shchirina-Éingorn and I.I. Kritskaya, Izv. Akad. Nauk SSR, Ser. Khim. (1977) 2345.
11. A. Mendoza and D.S. Matteson, J. Organometal. Chem., 152 (1978) 1.
12. P. Royo and R. Serrano, J. Organometal. Chem., 144 (1978) 33.
13. J.S. Thayer, Synth. React. Inorg. Metal-Org. Chem., 8 (1978) 371.
14. E.J. Bulten and H.A. Budding, J. Organometal. Chem., 153 (1978) 305.
15. M.H. Abraham and M.R. Sedaghat-Herati, J. Chem. Soc., Perkin Trans. II (1978) 729.
16. H.-P. Abicht and K. Issleib, J. Organometal. Chem., 149 (1978) 209.
17. A.N. Nesmeyanov, E.G. Perevalova, L.I. Leont'eva, S.A. Eremin and E.A. Zhdanova, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 2557.
18. P.J. Craig and S.F. Morton, J. Organometal. Chem., 145 (1978) 79.
19. A.v. Rumohr and W. Sundermeyer, Z. anorg. allg. Chem., 443 (1978) 37.
20. F. Calas, P. Moreau and A. Commeyras, J. Fluorine Chem., 12 (1978) 67.

21. W.F. Carroll, Jr. and D.G. Peters, J. Org. Chem., 43 (1978) 4633.

22. A.J. Fry and D. Herr, Tetrahedron Lett. (1978) 1721.

23. A.J. Fry, G.S. Ginsburg and R.A. Parente, J. Chem. Soc. Chem. Commun. (1978) 1040.

24. M.D. Rausch and R.E. Gloth, J. Organometal. Chem., 153 (1978) 59.

25. D. Seyferth and J.S. Merola, J. Organometal Chem., 160 (1978) 275.

26. J. Barluenga, F.J. Fañanas, M. Yus and G. Asenso, Tetrahedron Lett. (1978) 2015.

27. J.M. Burlitch and R.C. Winterton, J. Organometal. Chem., 159 (1978) 299.

28. D.M. Heinekey and S.R. Stobart, Inorg. Chem., 17 (1978) 1463.

29. H.D. Johnson, T.W. Hartford and C.W. Spangler, J. Chem. Soc. Chem. Commun. (1978) 242.

30. V.I. Shcherbakov, I.K. Grigor'eva and O.S. D'yachkovskaya, Zh. Obshch. Khim., 48 (1978) 1148.

31. R.J. Lagow, R. Eujen, L.I. Gerchman and J.A. Morrison, J. Am. Chem. Soc., 100 (1978) 1722.

32. R. Eujen and R.J. Lagow, J. Chem. Soc., Dalton Trans. (1978) 541.

33. A.N. Nesmeyanov, E.G. Perevalova, O.B. Afanasova, M.V. Tolstaya and K.I. Grandberg, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1118.

34. A.N. Nesmeyanov and A.Z. Rubezhov, J. Organometal. Chem., 164 (1978) 259.

35. R.C. Larock and M.A. Mitchell, J. Am. Chem. Soc., 100 (1978) 180.

36. J.K. Jawad and R.J. Puddephatt, Inorg. Chim. Acta, 31 (1978) L391.

37. V.V. Bashilov, V.I. Sokolov, G.Z. Suleimanov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 2562.

38. O.A. Reutov, V.I. Sokolov, G.Z. Suleimanov and V.V. Bashilov, J. Organometal. Chem., 160 (1978) 7.

39. V.I. Sokolov and V.V. Bashilov, Zh. Obshch. Khim., 14 (1978) 1114.

40. G.K. Anderson and R.J. Cross, J. Chem. Soc. Chem. Commun. (1978) 819.

41. J. Browning, P.L. Goggin, R.J. Goodfellow, N.W. Hurst, L.G. Mallinson and M. Murray, J. Chem. Soc., Dalton Trans. (1978) 872.

42. J. Kuyper, Inorg. Chem., 17 (1978) 1458.

43. G.B. Deacon and A.J. Koplick, J. Organometal. Chem., 146 (1978) C43.

44. D. Seyferth, J.S. Merola and C.S. Eschbach, J. Am. Chem. Soc., 100 (1978) 4124.

45. R.C. Larock and J.C. Bernhardt, J. Org. Chem., 43 (1978) 710.

46. R.C. Larock, J.C. Bernhardt and R.J. Driggs, J. Organometal. Chem., 156 (1978) 45.

47. R.C. Larock and B. Riefling, J. Org. Chem., 43 (1978) 1468.

48. R.C. Larock, B. Riefling and C.A. Fellows, J. Org. Chem., 43 (1978) 131.

49. T. Arai and G.D. Daves, Jr., J. Am. Chem. Soc., 100 (1978) 287.

50. R.N. Butler, A.B. Hanahoe and W.B. King, J. Chem. Soc., Perkin Trans. I (1978) 881.

51. R.N. Butler and A.B. Hanahoe, Chem. Ind. (London) (1978) 39.

52. R.J. Ferrier and R.H. Furneaux, Carbohydrate Res., 57 (1977) 73.

53. B. Giese and J. Meister, Angew. Chem., 90 (1978) 636.

54. P. Hildebrand, G. Plinke, J.F.M. Oth and G. Schröder, Chem. Ber., 111 (1978) 107.

55. J.B. Lambert, K. Kobayashi and P.H. Mueller, Tetrahedron Lett. (1978) 4253.

56. M.K. Meilahn, D.K. Olsen, W.J. Brittain and R.T. Anders, J. Org. Chem., 43 (1978) 1346.

57. C.W. Martin, P.R. Lund, E. Rapp and J.A. Landgrebe, J. Org. Chem., 43 (1978) 1071.

58. R.J. Wroczynski, L.D. Iroff and K. Mislow, J. Org. Chem., 43 (1978) 4236.

59. J. Escudie, C. Couret and J. Satgé, Bull. Soc. Chim. France II (1978) 361.

60. V.I. Sokolov, V.V. Bashilov and O.A. Reutov, J. Organometal. Chem., 162 (1978) 271.

61. Yu. S. Shabarov, S.S. Mochalov, T.S. Oretskaya and V.V. Karpova, J. Organometal. Chem., 150 (1978) 7.

62. J.A. Soderquist and K.L. Thompson, J. Organometal. Chem., 159 (1978) 237.

63. S. Nishida, T. Fujioka and N. Shimizu, J. Organometal. Chem., 156 (1978) 37.

64. Y. Senda, S. Kamiyama and S. Imaizumi, J. Chem. Soc., Perkin Trans. I (1978) 530.

65. H.C. Brown and W.J. Hammar, Tetrahedron, 34 (1978) 3405.

66. N.A. Belikova, S.A. Lermontov, T.I. Pekhk, E.T. Lippmaa and A.F. Plate, Zh. Org. Khim.,14 (1978) 884.

67. E.V. Skorobogatova, L.N. Povelikina and V.R. Kartshov, Zh. Org. Khim., 14 (1978) 663.

68. S.V. Govindan and S.C. Bhattacharyya, Indian J. Chem., 16 (1978) 1.

69. S.N. Suryawanshi and U. Ramdas Nayak, Tetrahedron Lett. (1978) 4425.

70. T. Hosokawa, S. Miyagi, S.-I. Murahashi, A. Sonoda, Y. Matsuura, S. Tanimoto and M. Kakudo, J. Org. Chem., 43 (1978) 719.

71. J. Barluenga, C. Najera and M. Yus, Synthesis (1978) 911.

72. A.J. Bloodworth and M.E. Loveitt, J. Chem. Soc., Perkin Trans. I (1978) 522.

73. A.J. Bloodworth and J.A. Khan, Tetrahedron Lett. (1978) 3075.

74. W. Adam, A.J. Bloodworth, H.J. Eggelte and M.E. Loveitt, Angew Chem., 90 (1978) 216.

75. W. Adam and K. Sakanishi, J. Am. Chem. Soc., 100 (1978) 3935.

76. J.R. Nixon, M.A. Cudd and N.A. Porter, J. Org. Chem., 43 (1978) 4048.

77. D.K. Bates and M.C. Jones, J. Org. Chem., 43 (1978) 3775.

78. C. Battistini, P. Crotti, B. Macchia, F. Macchia and C.H. De Puy, J. Org. Chem., 43 (1978) 1400.

79. V.V. Razin and M.V. Eremenko, Zh. Org. Khim., 14 (1978) 1113.

80. S.N. Suryawanshi and U. Ramdas Nayak, Tetrahedron Lett. (1978) 465.

81. L.C. Damude and P.A.W. Dean, J. Chem. Soc. Chem. Commun. (1978) 1083.

82. A.G. Milaev and O. Yu. Okhlobystin, Zh. Obshch. Khim., 48 (1978) 469.

83. E.G. Perevalova,E.V. Shumilina and L.I. Leont'eva, Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 1438.

84. P.V. Roling and M.D. Rausch, Synth. React. Inorg. Metal.-Org. Chem., 8 (1978) 83.

85. R.N. Butler and A.M. O'Donohue, Tetrahedron Lett. (1978) 275.

86. G.B. Deacon and D. Tunaley, J. Organometal. Chem., 156 (1978) 403.

87. T.B. Patrick and T.-T. Wu, J. Org. Chem., 43 (1978) 1506.

88. M.A. Kazankova, I.G. Trostyanskaya, T.Ya. Satina and I.F. Lutsenko, Zh. Obschch. Khim., 48 (1978) 301.

89. T. Izumi and S.I. Miller, J. Org. Chem., 43 (1978) 871.

90. E.K.S. Liu and R.J. Lagow, J. Organometal. Chem., 145 (1978) 167.

91. J. Barluenga, A. Ara, G. Asensio and M. Yus, Anal. Quim., 74 (1978) 455.

92. J. Barluenga, J.M. Concellon, A. Ara, G. Asensio and M. Yus, Anal. Quim., 74 (1978) 785.

93. J. Barluenga, J.M. Concellon, G. Asensio and M. Yus, Anal. Quim., 74 (1978) 512.

94. V.V. Bashilov, V.I. Sokolov and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 1081.

95. A.J. Bloodworth and R.A. Savva, J. Organometal. Chem., 152 (1978) C29.

96. P.L. Yadav, V. Ramakrishna and N.K. Jha, Indian J. Chem. A, 16 (1978) 623.

97. S. Uemura, A. Toshimitsu, M. Okana, T. Kawamura, T. Yonezawa and K. Ichikawa, J. Chem. Soc., Chem. Commun. (1978) 65.

98. E.V. Uglova, Yu. K. Grishin and O.A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1977) 2478.

99. R.A. Jackson and D.W. O'Neill, J. Chem. Soc., Perkin Trans. II (1978) 509.

100. G.A. Razuvaev, S.F. Zhil'tsov, V.A. Sokolova, L.M. Mazanova and Yu. D. Semchikov, Dokl. Akad. Nauk SSSR, 239 (1978) 106.

101. M. Jawaid, F. Ingman, H.H. Liem and T. Wallin, Acta. Chem. Scand. A, 32 (1978) 7.

102. M. Niitsu, T. Manri and N. Iritani, Bull. Chem. Soc. Japan, 51 (1978) 2165.

103. K. Stanley, J. Martin, J. Schnittker, R. Smith and M.C. Baird, Inorg. Chim. Acta, 27 (1978) L111.

104. M. Jawaid, F. Ingman and D.H. Liem, Acta. Chem. Scand. A, 32 (1978) 333.

105. M. Jawaid, Talanta, 25 (1978) 215.

106. A.V. Fokin, V.A. Komarov, A.F. Kolomiets, A.I. Rapkin and T.M. Potarina, Izv. Adad. Nauk SSSR, Ser. Khim. (1978) 707.

107. S.D. Morse, K.A. Laurence, G.H. Sprenger and J.M. Shreeve, J. Fluorine Chem., 11 (1978) 327.

108. R.J. Bertino, G.B. Deacon and J.M. Miller, Austral. J. Chem., 31 (1978) 527.

109. A.J. Canty, R. Kishimoto and R.K. Tyson, Austral. J. Chem., 31 (1978) 671.

110. A.J. Canty and R.K. Tyson, Inorg. Chim. Acta, 29 (1978) 227.

111. O.A. Reutov, V.I. Rozenberg, V.A. Nikanorov and A.Z. Kreindlin, Dokl. Akad. Nauk SSSR, 239 (1978) 1371.

112. R.C. Thapliyal and J.L. Maddocks, J. Chromtog., 160 (1978) 239.

113. D.L. Rabenstein and C.A. Evans, Bioinorg. Chem., 8 (1978) 107.

114. A. Haas and M. Lieb, Chem. Ber., 111 (1978) 2891.

115. Y. Sugiura, Y. Tamai and H. Tanaka, Bioinorg. Chem., 9 (1978) 167.

116. N.S. Dance and C.W.H. Jones, J. Organometal. Chem., 152 (1978) 175.

117. I. Sarraje and J. Lorberth, J. Organometal. Chem., 146 (1978) 113.

118. A.J. Canty, M. Fyfe and B.M. Gatehouse, Inorg. Chem., 17 (1978) 1467.

119. A.J. Canty, private communication.

120. A.M. Khmaruk, T.V. Kovalevskaya and A.M. Pinchuk, Zh. Obshch. Khim., 48 (1978) 625.

121. P. Peringer, Z. Naturf., 33b (1978) 1091.

122. D.N. Kravtsov, A.N. Nesmeyanov, L.A. Fedorov, E.I. Fedin, A.S. Peregudov, E.V. Borisov, P.O. Okulevich and S.A. Postovoi, Dokl. Akad. Nauk SSSR, 242 (1978) 347.

123. V.I. Bregadze, V.Ts. Kampel', A.Ya. Usyatinskii and N.N. Godovikov, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1467.

124. V.I. Bregadze, V.Ts. Kampel', A.Ya. Usyatinskii and N.N. Godovikov, J. Organometal. Chem., 154 (1978) C1.

125. L.I. Zakharkin and I.V. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 1226.

126. V.I. Bregadze, V.Ts. Kampel' and N.N. Godovikov, J. Organometal. Chem., 157 (1978) C1; Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 1951.

127. L.A. Leites, L.E. Vinogradova, V.I. Bregadze, V.Ts. Kampel' and A.Ya. Usiatinsky, Inorg. Chim. Acta, 31 (1978) L467.

128. T.N. Mitchell and H.C. Marsmann, J. Organometal. Chem., 150 (1978) 171.

129. R.J.P. Corriu, G.F. Lanneau, D. Leclerq and D. Samate, J. Organometal. Chem., 144 (1978) 155.

130. M. Ziebarth and W.P. Neumann, Justus Liebigs Ann. Chem. (1978) 1765.

131. W.P. Neumann and F. Werner, Chem. Ber., 111 (1978) 3904.

132. K. Reuter and W.P. Neumann, Tetrahedron Lett. (1978) 5235.

133. E.N. Gladyshev, P.Ya. Bayushkin and V.S. Sokolov, Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 685.

134. O.A. Kruglaya, L.I. Belousova, N.P. Aktaev, G.A. Sokol'skii and N.S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 2800.

135. O.A. Kruglaya, L.I. Belousova and N.S. Vyazankin, Zh. Obshch. Khim., 48 (1978) 1430.

136. L. Rösch and W. Erb, Angew. Chem., 90 (1978) 631.

137. G.A. Razuvaev, V.N. Latyaeva, L.I. Vyshinskaya, A.V. Malysheva and G.A. Vasil'eva, Dokl. Akad. SSSR, 237 (1977) 605.

138. M.N. Bochkarev, N.I. Gur'ev and G.A. Razuvaev, J. Organometal. Chem., 162 (1978) 289.

139. D.P. Graddon and J. Mondal, J. Organometal. Chem., 160 (1978) 377.

140. D.P. Graddon and J. Mondal, J. Organometal. Chem., 159 (1978) 9.

141. I.S. Ahuja, R. Singh and C.P. Rai, J. Coord. Chem., 8 (1978) 117.

142. D.J. Gardiner, A.H. Haji and B.P. Straughan, J. Mol. Struct., 49 (1978) 301.

143. D.J. Gardiner, A.H. Haji and B.P. Straughan, J. Chem. Soc., Dalton Trans. (1978) 705.

144. P.L. Goggin, R.J. Goodfellow and N.W. Hurst, J. Chem. Soc., Dalton Trans. (1978) 561.

145. L.M. Epshtein, L.D. Ashkinadze, L.S. Golovchenko, V.M. Pachevskaya and D.N. Kravtsov, Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 1300.

146. A.V. Shabanov, V.A. Kuznetsov, A.N. Egorochkin, S.F. Zhil'tsov and G.A. Razuvaev, Dokl. Akad. Nauk SSSR, 239 (1978) 617.

147. E. Vander Donckt and C. Von Vooren, J. Chem. Soc., Faraday Trans. I, 74 (1978) 827.

148. H. Oberhammer, J. Mol. Struct., 48 (1978) 389.

149. D.J. Brauer, H. Bürger, G. Pawelke, K.-H. Flegler and A. Haas, J. Organometal. Chem., 160 (1978) 389.

150. D. Grdenić, M. Sikirica and B. Korpar-Colig, J. Organometal. Chem., 153 (1978) 1.

151. J. Halfpenny, R.W.H. Small and F.G. Thorpe. Acta. Cryst. B, 34 (1978) 3077.

152. J.L. Atwood, L.G. Canada, A.N.K. Lau, A.G. Ludwick and L.M. Ludwick, J. Chem. Soc., Dalton Trans. (1978) 1573.

153. D.S. Brown, A.G. Massey and D.A. Wickens, Acta. Cryst. B, 34 (1978) 1695.

154. N.C. Baenziger, R.M. Flynn, D.C. Swenson and N.L. Holy, Acta Cryst. B, 34 (1978) 2300.

155. N.G. Bokii, Yu. T. Struchkov, V.N. Kalinin and L.I. Zakharkin, Zh. Strukt. Khim., 19 (1978) 380.

156. R.T.C. Brownlee, A.J. Canty and M.F. Mackay, Austral. J. Chem., 31 (1978) 1933.

157. A.J. Canty, N. Chaichit, B.M. Gatehouse and A. Marker, Acta Cryst. B, 34 (1978) 3229.

158. C. Chieh, Can. J. Chem., 56 (1978) 560.

159. N.W. Alcock, P.A. Lampe and P. Moore, J. Chem. Soc., Dalton Trans. (1978) 1324.

160. A. Medici, G. Rosini, E.F. Serantoni and L.R. di Sanseverino, J. Chem. Soc., Perkin Trans. I (1978) 1110.

161. A. Ruiz-Amil, S. Martinez-Carrera and S. Garcia-Blanco, Acta Cryst. B, 34 (1978) 2711.

162. C.L. Raston, B.W. Skelton and A.H. White, Austral. J. Chem., 31 (1978) 537.

163. E.A. Sadurski, W.H. Ilsey, R.D. Thomas, M.D. Glick and J.P. Oliver, J. Am. Chem. Soc., 100 (1978) 7761.

164. A.J. Canty, C.L. Raston and A.H. White, Austral. J. Chem., 31 (1978) 677.

165. J. Halfpenny, R.W.H. Small and F.G. Thorpe, Acta Cryst. B, 34 (1978) 3075.

166. J. Halfpenny and R.W.H. Small, Acta Cryst. B, 34 (1978) 3758.

167. P.L. Goggin, R.J. Goodfellow, K. Kessler and A.M. Prescott, J. Chem. Soc., Dalton Trans. (1978) 328.

168. P.L. Goggin and N.W. Hurst, J. Chem. Res. (1978) (S) 388, (M) 4713.

169. J. Mink and P.L. Goggin, J. Organometal. Chem., 156 (1978) 317.

170. D.M. Adams and D.J. Hills, J. Chem. Soc., Dalton Trans. (1978) 776.

171. P.L. Goggin and D.M. McEwan, J. Chem. Res. (1978) (S) 171; (M) 2253.

172. L.M. Epshtein, V.L. Beloborodov, L.D. Ashkinadze, E.M. Rokhlina, S.I. Pombrik, D.N. Kravtsov and L.A. Kazitsyna, J. Organometal. Chem., 162 (1978) C1.

173. L.M. Epshtein, V.L. Beloborodov, L.D. Ashkinadze, L.S. Golovchenko, V.M. Pachevskaya, D.N. Kravtsov and L.A. Kazitsyna, J. Organometal. Chem., 162 (1978) C5.

174. V.I. Stanko, V.V. Khrapov, T.V. Klimova, T.A. Babushkina and T.P. Klimova, Zh. Obshch. Khim., 48 (1978) 368.

175. J. Jokisaari and K. Raisanen, Mol. Phys., 36 (1978) 113.

176. J.L. Sudmeier, R.R. Birge and T.G. Perkins, J. Mag. Reson., 30 (1978) 491.

177. A.J. Canty, A. Marker, P. Barron and P.C. Healy, J. Organometal. Chem., 144 (1978) 371.

178. Yu. A. Strelenko, Yu. G. Bundel', F.H. Kasumov, V.I. Rozenberg, O.A. Reutov and Yu. A. Ustynyuk, J. Organometal. Chem., 159 (1978) 131.

179. S.P. Gubin, Z.A. Rubezhov and L.I. Voronchikina, J. Organometal. Chem., 149 (1978) 123.

180. E.N. Gladyshev, P.Ya. Bayushkin, G.A. Abakumov and E.S. Klimov, Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 176.

181. G. Wulfsberg, R.J.C. Brown, J. Graves, D. Essig, T. Bonner and M. Lorber, Inorg. Chem., 17 (1978) 3426.

182. L.L. Coatsworth, G.M. Bancroft, D.K. Creber, R.J.D. Lazier and P.W.M. Jacobs, J. Electron. Spec., 13 (1978) 395.

183. S. Cradock and W. Duncan, J. Chem. Soc., Faraday Trans. II (1978) 194.

184. V. Luckow and H.A. Rüssell, J. Chromatog., 150 (1978) 187.

185. J.-P. Schmit and D.R. Wiles, Can. J. Chem., 56 (1978) 1956.

186. J. Starý, K. Kratzer and J. Prašilová, Anal. Chim. Acta, 100 (1978) 627.

187. D.C. Stuart, Anal. Chim. Acta, 96 (1978) 83.

188. K. Tajima and F. Kai, Chem. Lett. (1978) 201.

189. K. Tajima and F. Kai, J. Chem. Eng. Data, 23 (1978) 234.

190. D.A. Bochvar and Yu.A. Borisov, Izv. Akad. Nauk SSSR, Ser. Khim. (1978) 1166.

191. P. Svejda, A.H. Maki and R.R. Anderson, J. Am. Chem. Soc., 100 (1978) 7138.

192. B.J. Farey, L.A. Nelson and M.G. Rolph, The Analyst, 103 (1978) 656.

193. G.A. Nyssen and M.M. Jones, Chem. Tech., 8 (1978) 546.

194. "AMBORANE Reductive Resins", data sheet, Alfa Division, Ventron Corp.