MERCURY

ANNUAL SURVEY COVERING THE YEAR 1975

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Mercury, Annual Survey covering the year 1974 see J. Organometal. Chem., 98(1975)133-293.

I. REVIEWS AND BOOKS

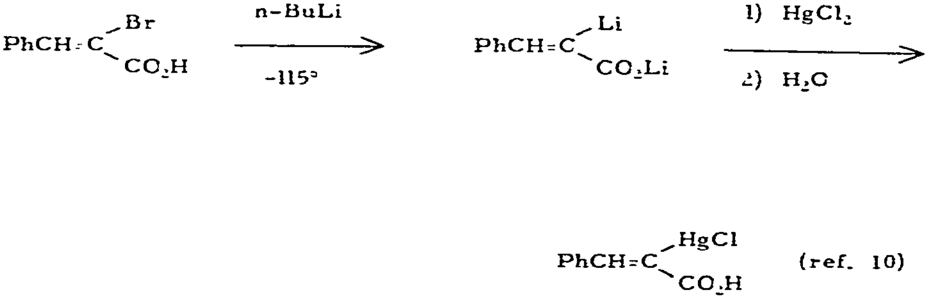
Volume 12 of "Comprehensive Chemical Kinetics" (1) covers the subject of electrophilic substitution at a saturated carbon atom. Included in the discussion is electrophilic cleavage of the mercury-carbon bond. For a review of this book, see (2). The preparation of some α-fluoroalkylmercury compounds and their use as precursors for fluorinated carbenes has been reviewed in the second volume of the two volume set on "Carbenes" (3).

Articles in review journals have covered the following topics in organomercury chemistry:

- The structural chemistry of organomercury compounds (4)
- Electrochemical synthesis of organomercury compounds (5)
- Application of aminomercuration in the synthesis of heterocyclic compounds (6)
- The liquid phase homolytic reactions of organomercurials (7)
- Reactions which involve organomercury(I) intermediates of the type RHg-HgR (8)
- The displacement of alkali metals from their organic derivatives by mercury (9).

2. PREPARATION OF ORGANOMERCURY COMPOUNDS

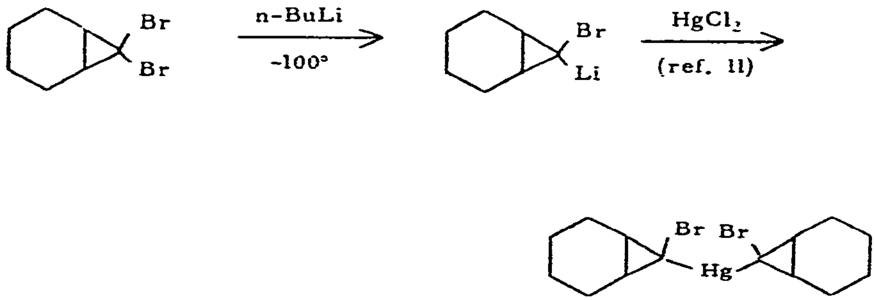
The reactions of elemental mercury and of inorganic mercury(II) compounds with organometallic derivatives of other elements continues to find useful application in the synthesis of organomercurials. Examples of the standard use of organolithium and Grignard reagents in the preparation of simple organomercury compounds will not be related, but some more special cases in which main group organometallic reagents were used deserve mention.



$$PhCH{=}C\begin{smallmatrix}Br\\ CO_2H\end{smallmatrix} \xrightarrow[-115^\circ]{n\text{-}BuLi} PhCH{=}C\begin{smallmatrix}Li\\ CO_2Li\end{smallmatrix} \xrightarrow[2)\ H_2O]{1)\ HgCl_2} PhCH{=}C\begin{smallmatrix}HgCl\\ CO_2H\end{smallmatrix}$$

(ref. 10)

(mixture of cis and trans isomers)



A number of per- and polyfluorinated organomercurials were prepared by an anion route (12):

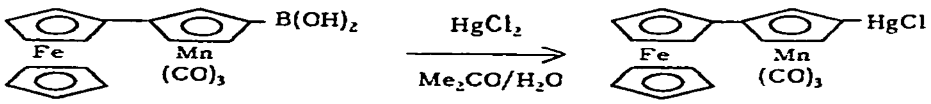
$$2\,(CF_3)_2C{=}CF_2 + 2\,KF + Hg(O_2CCF_3)_2 \xrightarrow{THF} [(CF_3)_3C]_2Hg + 2\,CF_3CO_2K$$

$$(CF_3)_2C{=}CF_2 + KF + CF_3HgO_2CCF_3 \xrightarrow{THF} CF_3HgC(CF_3)_3 + CF_3CO_2K$$

$$CF_3CBr{=}CF_2 + CsF + CF_3HgO_2CCF_3 \xrightarrow{THF} CF_3HgCBr(CF_3)_2 + CF_3CO_2Cs$$

$$CF_3C{\equiv}CCF_3 + CsF + Hg(O_2CCF_3)_2 \xrightarrow{DMF} [CF_3CF{=}C(CF_3)]_2Hg + CF_3CO_2Cs$$

Organometallic derivatives of Group III elements also serve in the preparation of organomercury compounds:



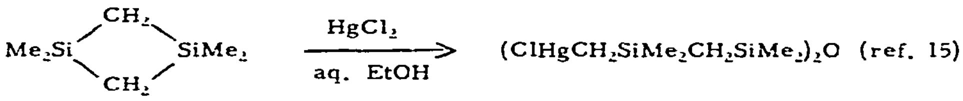
(ref. 13)

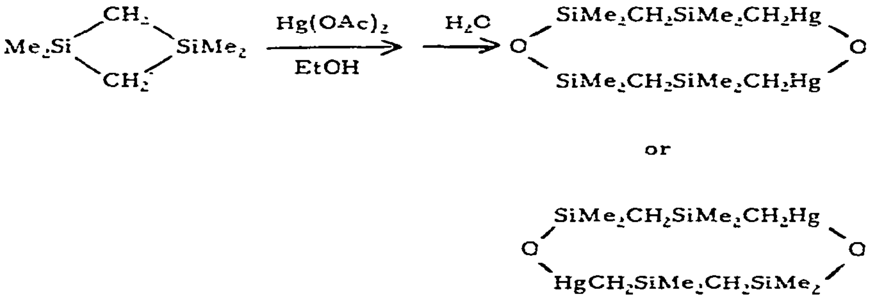
$$(ZC_6H_4)_2TlCl + Hg \longrightarrow (ZC_6H_4)_2Hg + TlCl$$

(Z = p-OMe, p-Me, H,
p-Cl, p-AcO)

The mechanism of this reaction was studied by means of polarography and chronopotentiometry (14). Intermetallic cations of type $ArTl^{+}HgR$ were shown to be intermediates.

English and Russian groups have studied reactions of mercury(II) compounds with sila- and disilacyclobutanes in which the silacarbocyclic compounds underwent ring opening to give silyl-substituted mercurials.

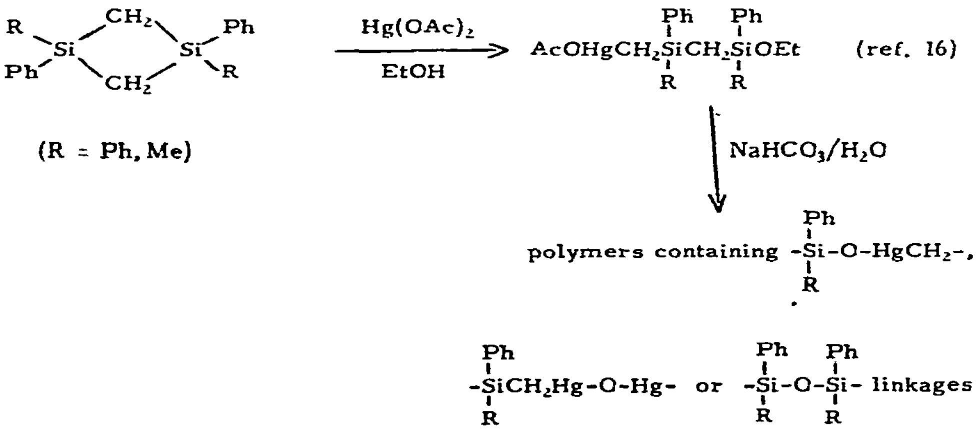


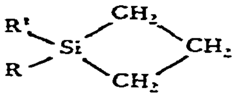


1

2

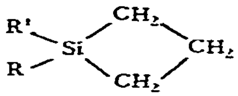
The available spectroscopic data did not allow the investigators to distinguish between 1 and 2 as the structure of the product (15).





$\xrightarrow[MeOH]{Hg(NO_3)_2}$ $(O_3NHgCH_2CH_2CH_2SiRR')_2O$ (ref. 17)

but:



$\xrightarrow[H_2O]{Hg(NO_3)_2}$ $HO(SiRR'CH_2CH_2CH_2)_nHgNO_3$

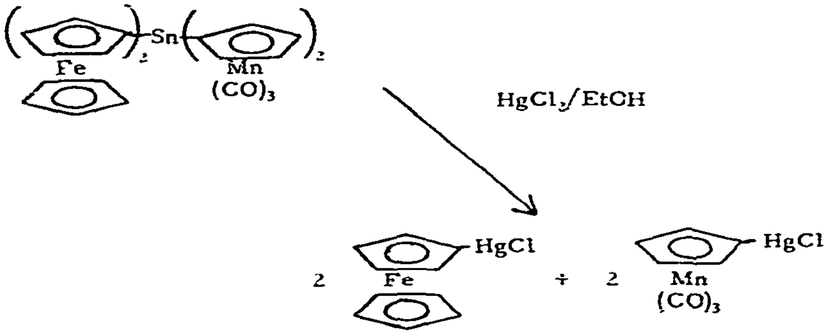
$+$

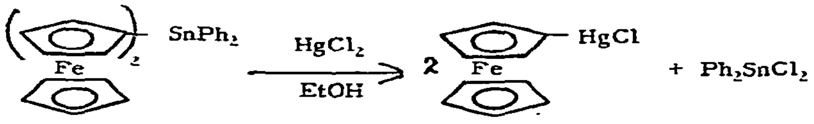
$O[(SiRR'CH_2CH_2CH_2)_nHgNO_3]_2$

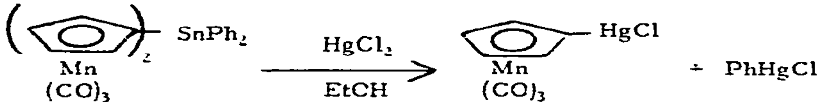
$n = 1\text{–}4$

The same difference in behavior toward $Hg(NO_3)_2$ in methanol and $Hg(NO_3)_2$ in aqueous medium was found in the case of 1,3-disilacyclobutanes (17).

Organotin derivatives of some metallocenes underwent facile Sn–C cleavage (18):







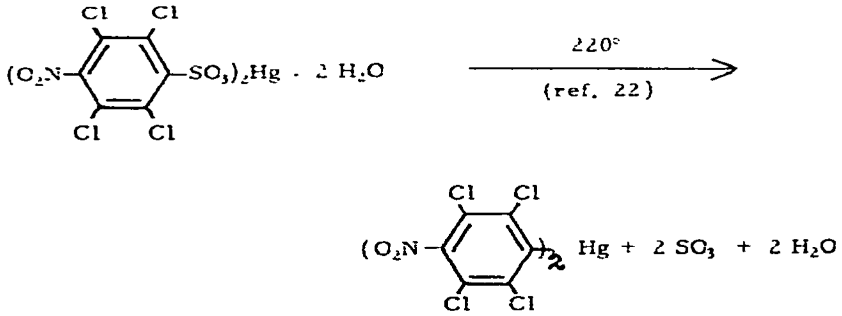
The biologically important transfer of methyl groups from cobalt complexes to Hg(II) has received further study. Such transfer of methyl groups to Hg(II) from a series of methylcobalt(III) chelate complexes has been the subject of a kinetic study (19) and the role of the anion in HgX_2 in the demethylation of methylcobalamin has received attention (20).

Decarboxylation, desulfonation and desulfination reactions continue to find useful application in the synthesis of organomercurials. Deacon has extended the scope of his investigations in this area to the synthesis of perbromo-, tetrachloronitro- and polyfluorophenylmercury compounds:

$$(C_6Br_5CO_2)_2Hg \xrightarrow{\Delta,\ py} (C_6Br_5)_2Hg + 2\ CO_2 \qquad \text{(ref. 21)}$$

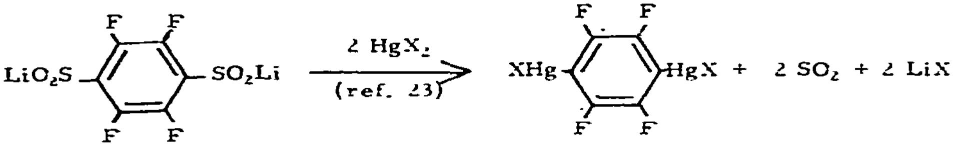
(Bis(pentabromophenyl)mercury is stable to at least its mp of 406°).

$$PhHgO_2CC_6Br_5 \xrightarrow{\Delta,\ py} PhHgC_6Br_5 + CO_2 \qquad \text{(ref. 21)}$$

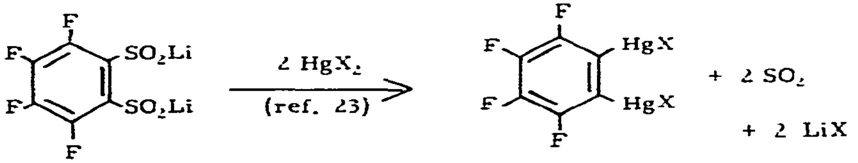


$$ArSO_2Li + HgX_2 \xrightarrow[\text{(ref. 23)}]{H_2O,\ \text{room temp.}} ArHgX + SO_2 + LiX$$

(Ar = C_6F_5, o, m,
and p-HC_6F_4;
X = Cl, Br, OAc)



(X = Cl, Br, OAc)



(X = Cl, Br)

$$2\ ArSO_2Li + HgX_2 \xrightarrow[\substack{\text{room temp.}\\ \text{(ref. 23)}}]{Me_3COH/H_2O} Ar_2Hg + 2\ SO_2 + 2\ LiX$$

(Ar = C_6F_5, m, p-
HC_6F_4)

The peroxide-induced decarboxylation of mercury(II) carboxylates also has received further attention, with emphasis on mechanistic aspects. The scope of this reaction has been extended to the synthesis of large ring organomercurials (24) :

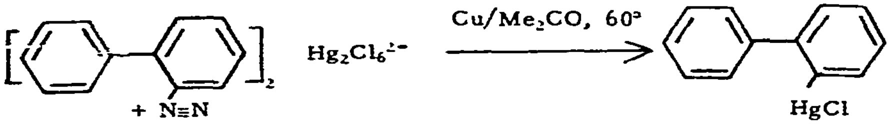
$$(RCO_2)_2Hg \xrightarrow[C_6H_6,\ 80^\circ]{Bz_2O_2\ \text{or UV}} \xrightarrow{KBr} RHgBr$$

(R = cyclo-$C_{11}H_{21}$ and cyclo-$C_{12}H_{23}$)

Three papers by Reutov and his coworkers have dealt with details of the known free radical mechanism of such reactions (25-27). It was found that in the diacyl peroxide-induced reactions in some instances it is the organic group of the peroxide which in the main provides the organomercury product. This was shown by ^{13}C labelling in the $(cyclo\text{-}C_6H_{11}CO_2)_2Hg$/cyclo-$C_6H_{11}C(O)OOC(O)C_6H_{11}$-cyclo system (26). The fact that the chief organomercury product in the $(cyclo\text{-}C_5H_9CO_2)_2Hg$/cyclo-$C_6H_{11}C(O)OOC(O)C_6H_{11}$-cyclo reaction was the cyclohexylmercurial lent support to this idea, but in the $(cyclo\text{-}C_6H_{11}CO_2)_2Hg$/cyclo-$C_5H_9C(O)OOC(O)C_5H_9$-cyclo reaction the cyclohexylmercurial also was the major product (27). Clearly, these are complicated reactions in which the ease of formation and the stability of the carboxy and alkyl radicals involved play an important role. In any case, these are not simple decarboxylation reactions but involve S_H2 processes at mercury. The esters formed as byproducts in such reactions also were studied (25).

Other radical processes have served in the preparation of organomercury compounds. Thus trifluoromethyl radicals, generated by hexafluoroethane homolysis in a glow discharge, react with mercury vapor in a suitable reactor to give $(CF_3)_2Hg$ (28). A more effective synthesis of this compound was given by the reaction of CF_3 radicals (glow discharge) with mercuric iodide. Similar reactions with mercuric chloride and bromide resulted in formation of CF_3HgCl and CF_3HgBr, respectively (29).

The synthesis of arylmercurials via aryldiazonium salts also involves radical intermediates. A new example has been described (30):



The sunlight-induced methylation of mercuric acetate in aqueous acetic acid was found to be photosensitized in the presence of HgS. The actual photosensitizer is the polymeric sulfur obtained in the decomposition of mercuric sulfide (31).

New examples of the mercuration of functional aliphatic compounds have been reported.

$$\text{Hg(OAc)}_2 + (\text{CF}_3)_2\text{CHCN} \xrightarrow{\text{DMF}} \text{AcOHgC(CF}_3)_2\text{CN} + \text{HOAc} \qquad \text{(ref. 32)}$$

$$\text{Hg(OAc)}_2 + 2\,(\text{CF}_3)_2\text{CHCN} \xrightarrow[\text{(ref. 32)}]{20\%\ \text{aq. HOAc}} \text{Hg[C(CF}_3)_2\text{CN]}_2 + 2\ \text{HOAc}$$

Although the mercuration of aliphatic aldehydes is a long-known reaction, the structures of the products have remained obscure. Recent work by Aleksandrov et al. (33) has indicated a polymeric structure, $[\text{HCHg(CHR)CHO}]_n$. This result, based on IR and combustion analyses, does not seem entirely satisfactory, but the products were infusible, insoluble powders which were difficult to study.

An important reaction in synthetic organomercury chemistry is the redistribution reaction by which RHgX compounds are converted to symmetrical mercurials, R_2Hg. Halpern and Garti have studied this reaction in some detail. The process:

$$2\ \text{ArHgX} \xrightarrow[\text{aq./organic solvent}]{\text{chelating agent + nucleophile}} \text{Ar}_2\text{Hg} + \text{HgX}_2$$

was studied; the chelating agent and the nucleophile were varied and the Na_4EDTA/NH_3 system was found to give the best results (34). Most of the investigations were carried out with phenylmercury salts, but other diarylmercury compounds were prepared by this procedure. Electron-donating substituents (MeO, Me, Me_2N) on the aryl ring of ArHgX increased both the reaction rate and Ar_2Hg yield. Electron-withdrawing substituents (Cl, Br) had the opposite effect. The presence of OH, NH_2 or COOH substituents on the aryl ring of ArHgX inhibited the disproportionation reaction. Such symmetrizations can be effected in the absence of an auxiliary nucleophile in acidic or basic medium, depending on the substituents on the aryl ring (35). The reactions do not take place in the absence of a chelating agent such as Na_4EDTA. The mechanism of the symmetrization reaction in the presence of chelating agents has been studied (36). The following steps were proposed:

a) ionization of the arylmercury compound:

$$ArHgX \rightleftharpoons ArHg^{+} + X^{-}$$

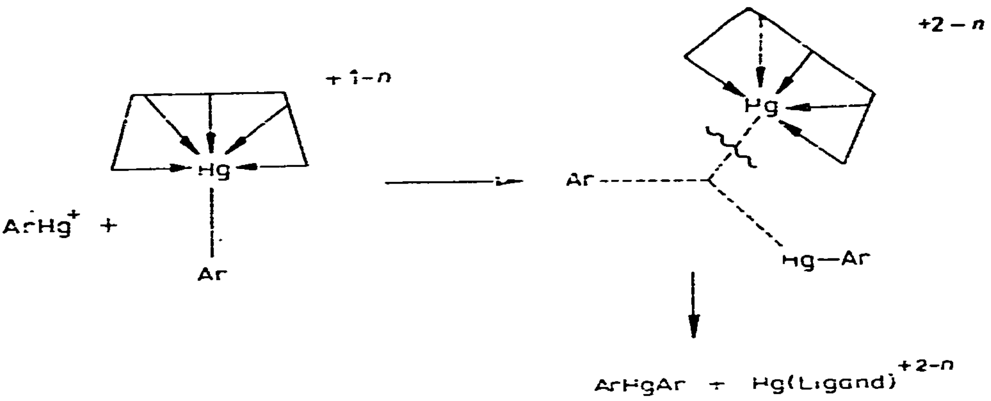
b) complexation of the arylmercury cation with the chelating agent:

$$ArHg^{+} + Che^{n-} \rightleftharpoons ArHgChe^{+1-n}$$

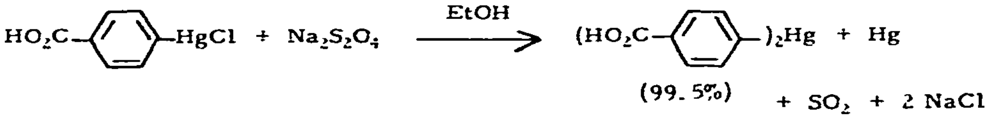
c) electrophilic substitution at the C-Hg bond:

$$ArHg^{+} + ArHgChe^{+1-n} \longrightarrow ArHgAr + HgChe^{+2-n}$$

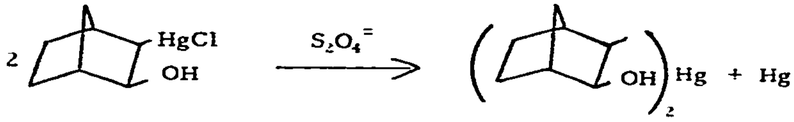
The rate-and yield-enhancing properties of the added nucleophile are important in step (c). A three-center, two-electron transition state was suggested:



High yield recyclization symmetrization processes for water-soluble and water-insoluble arylmercuric salts have been developed and are illustrated in Fig. 1 and 2 (37). Symmetrization also has been found to be effectively promoted by sodium dithionite, a strong reducing agent (38):



This reaction proceeds with retention of configuration at carbon:



A non-radical reaction mechanism seems indicated.

Thermal symmetrization has been observed with pentabromophenylmercuric halides (21):

$$2\ C_6Br_5HgX \xrightarrow{> 250^\circ \text{ (below mp)}} (C_6Br_5)_2Hg + HgX_2$$

(X = Cl, Br)

(Continued on p. 187)

Figure 1. Flow sheet of the Recyclization Symmetrization Process for Water-Soluble Arylmercuric Salts

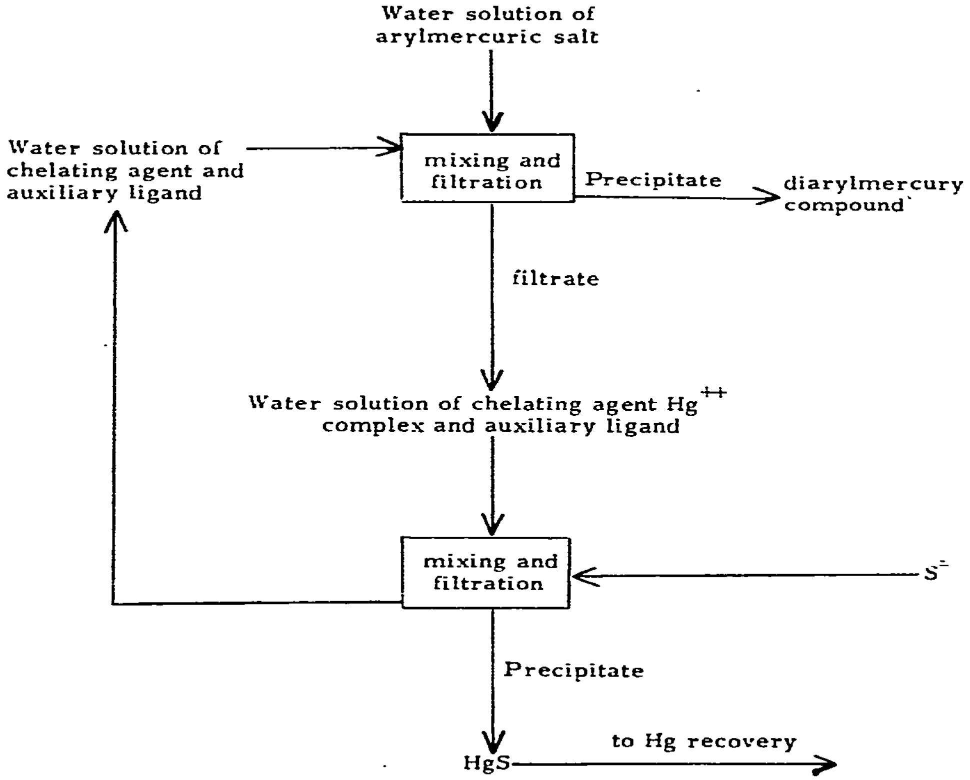
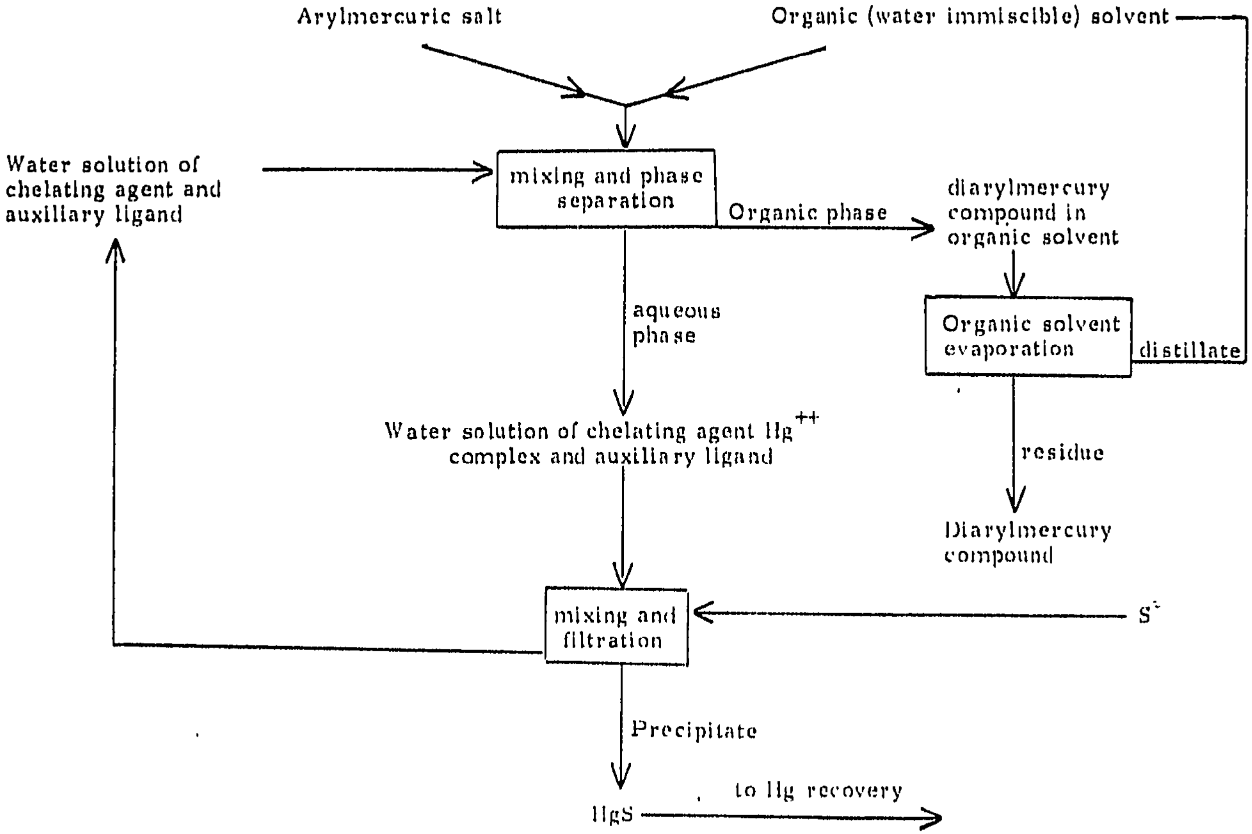


Figure 2. Flow Sheet of the Recyclization Process for Water-Insoluble Arylmercuric Salts



3. USE OF ORGANOMERCURY COMPOUNDS IN SYNTHESIS

A. Organomercury Compounds in Synthesis

Organomercurials continue to find occasional use in the synthesis of organometallic derivatives of other metals via reactions with metals or metal halides. Some examples reported recently follow below.

$$(PhCH_2)_2Hg \xrightarrow[Li^+,\ THF]{e^-\ pulse} PhCH_2Li \qquad (ref.\ 39)$$

$$(Me_3SiCH_2)_2Hg \xrightarrow{K} Me_3SiCH_2K \qquad (ref.\ 40)$$

(See also an earlier, more general report of this reaction: J. Organometal. Chem., 98 (1975) 151)

$$(PhCH_2)_2Hg \xrightarrow{Ba} (PhCH_2^-)_2\ Ba^{2+} \qquad (ref.\ 41)$$

$$R_2Hg + M + 2\ AlR'_3 \xrightarrow[xylene\ or\ heptane]{Et_2O\ or\ THF} M[AlR'_3R]_2 + Hg$$

(ref. 42)

(M = Ca, Sr, Ba;
R = Et, n-Pr, Ph, p-MeC$_6$H$_4$
R' = Et, n-Pr, Ph)

$$ArHgX + InX \longrightarrow ArInX_2 + Hg$$

$$Ar_2Hg + InX \longrightarrow Ar_2InX + Hg$$

$$2\ Ar_2Hg + HgX_2 + 2\ In \longrightarrow 2\ Ar_2InX + 3\ Hg$$

$$Ar_2Hg + HgX_2 + 2\ InX \longrightarrow 2\ ArInX_2 + 2\ Hg$$

The aryl groups included Ph, p-FC_6H_4, p-MeC_6H_4; mercuric chloride and bromide were used (43).

$$BrHgCH(Ph)CO_2Me + Me_3SiX \xrightarrow[\text{(ref. 44)}]{} PhCH{=}C(OMe)(OSiMe_3) + HgBrX$$

(cis/trans mixture)

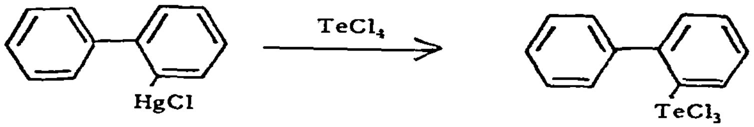
$$R_2Hg + SnCl_2 \xrightarrow{\text{DME or THF}} R_2SnCl_2 + Hg \qquad \text{(ref. 45)}$$

(60-92%)

(R = p-$Et_2NC_6H_4$,
p-$Me_2NC_6H_4$, p-$MeOC_6H_4$,
$C_5H_5FeC_5H_4$, $(OC)_3MnC_5H_4$,
α-thienyl)

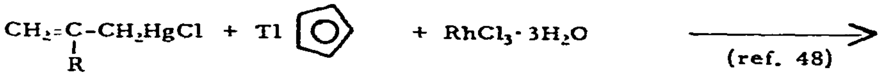
$$R_2Hg + SnF_2 \longrightarrow RSnF_3 \qquad \text{(ref. 46)}$$

(R = Et, n-Pr, n-Bu,
n-C_5H_{11}, n-C_6H_{13}



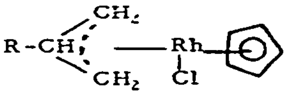
(ref. 47)

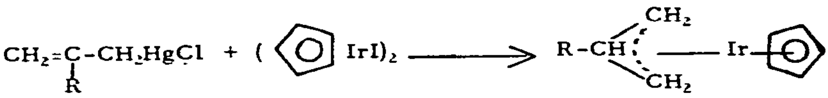
Organomercurials also have been used in the synthesis of some organo-transition metal complexes. Thus π-allyl complexes can be prepared via σ-allylmercuric halides:

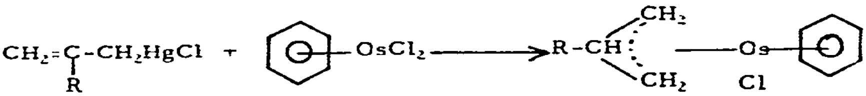


$$CH_2{=}\underset{R}{C}{-}CH_2HgCl + Tl \quad + RhCl_3\cdot 3H_2O \xrightarrow[\text{(ref. 48)}]{}$$

(R = H, Me)







(ref. 50)

Full details have been published concerning the oxidative addition of RHgX and R_2Hg compounds to zerovalent triphenylphosphine complexes of palladium and platinum (51) (cf. J. Organometal. Chem., 98 (1975) 155). Some examples follow:

$$(Ph_3P)_3Pt + p\text{-}MeC_5H_4HgBr \longrightarrow (Ph_3P)_2Pt(Br)C_6H_4Me\text{-}p$$

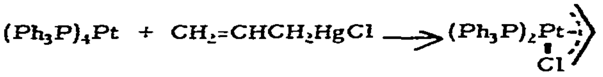
$$(Ph_3P)_3Pt + Ph_2Hg \longrightarrow (Ph_3P)_2PtPh_2$$

$$(Ph_3P)_3Pt + Hg(CH_2CO_2R)_2 \longrightarrow (Ph_3P)_2Pt(CH_2CO_2R)_2$$

(R = Me, i-Bu)

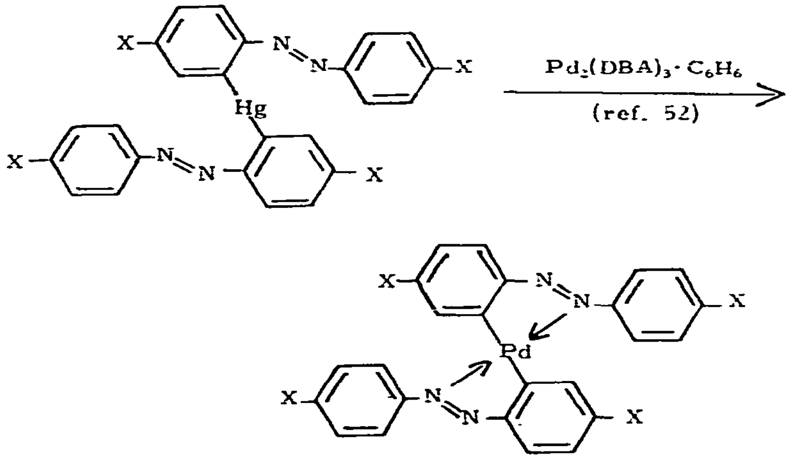
$$(Ph_3P)_4Pt + MeHgI \longrightarrow (Ph_3P)_2Pt(I)Me$$

$$(Ph_3P)_3Pt + (p\text{-}MeOC_6H_4)_2C{=}CHHgCl \longrightarrow (Ph_3P)_2Pt(Cl)CH{=}C(C_6H_4OMe)_2$$



$$(Ph_3P)_4Pt + (CF_3)_2Hg \longrightarrow (Ph_3P)_2Pt(CF_3)HgCF_3$$

$$Pd_2(DBA)_3 \cdot C_6H_6{}^{*} + \text{o-phen} + \text{p-}MeC_6H_4HgCl \longrightarrow \text{o-phen}Pd(Cl)C_6H_4Me\text{-p}$$



(Note some similar complexes reported in last year's Survey: J. Organometal. Chem., 98 (1975) 154).

The stereochemistry of the transfer of alkyl groups from mercury to palladium has been studied by two groups using olefin solvomercuration products with known configuration at the C-Hg bond. Both groups found that such reactions proceed with retention of configuration at carbon:

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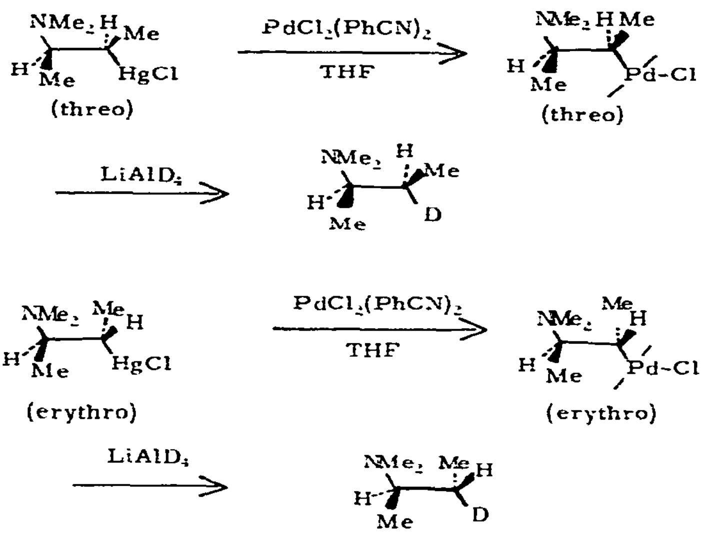
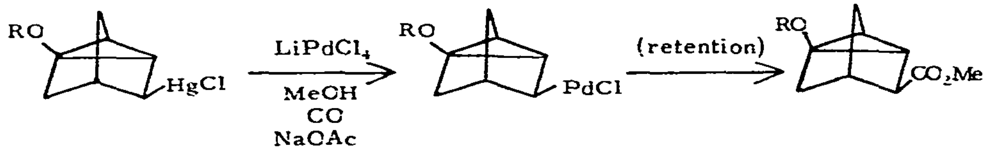
* DBA = dibenzylideneacetone



(ref. 53)



(ref. 54)

Two explanations were offered for this stereochemical course: (1) a four-center, bimolecular, electrophilic exchange of palladium for mercury or (2) an oxidative addition of the organomercury compound to a Pd(II) species with retention of configuration at carbon (54).

B. Organic Synthesis

Cleavage of the C-Hg bond with molecular halogens, or, in the case of iodine, with triiodide ion, has been used in the past to prepare organic halides not readily available by other routes. Some more examples of such reactions have been published.

$(C_6Br_5)_2Hg \xrightarrow{I_3^- \text{ in DMF}} 2\ C_6Br_5I + HgI_2$ (ref. 21)

$$(O_2NC_6Cl_4)_2Hg \xrightarrow{I_3^- \text{ in DMF}} 2\ O_2NC_6Cl_4I + HgI_2$$

(The o, m and p nitrotetrachlorophenylmercurials were cleaved in this way (22).

$$Hg[C(CF_3)_2CN]_2 \xrightarrow{X_2} 2\ (CF_3)_2C(CN)X + HgX_2 \qquad \text{(ref. 32)}$$

$(X = Cl, Br, I)$

Of special interest is the preparation of β-bromo peroxides by brominolysis of the peroxymercurials derived from diverse types of olefins (55). The results are shown in Table 1. A homolytic process appeared to be operative in the solvent used.

TABLE 1. Preparation of β-Bromo Peroxides (ref. 55)

$$R^1CH{=}CHR^2 + Hg(OAc)_2 + Me_3COOH \xrightarrow{KBr} R^1\underset{\displaystyle OOCMe_3}{CH}CH(HgBr)R^2 \xrightarrow{Br_2} R^1\underset{\displaystyle OOCMe_3}{CH}CH(Br)R^2$$

	β-Bromo Peroxide		
Parent Alkene	R^1	R^2	% Yield
C_2H_4	H	H	80
$CH_3CH{=}CH_2$	CH_3	H	81
cis-MeCH=CHMe	CH_3	CH_3	83
trans-EtCH=CHEt	Et	Et	87
cis-PhCH=CHPh	Ph	Ph	79
trans-PhCH=CHMe	Ph	Me	65
cyclohexene	$-(CH_2)_4-$		87
norborn-2-ene			87

Replacement of Hg by H in an organomercurial can be effected in many cases by simple protolysis, e.g.:

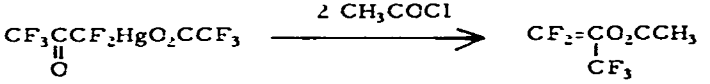
$$Hg[C(CF_3)_2CN]_2 \xrightarrow{HCl\ \text{or}\ H_2SO_4} HC(CF_3)_2CN \quad (70\text{-}95\%) \quad (\text{ref. } 32)$$

Solvomercuration products of olefins, however, undergo β -elimination on treatment with acids and so reductive procedures must be used, e.g., from last year's literature (56):

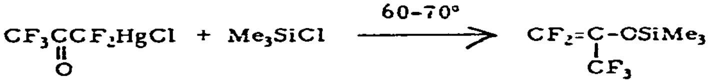
$$IHgCH_2CH_2OCH_2Ph \xrightarrow{2\%\ Na/Hg,\ D_2O} CH_2DCH_2OCH_2Ph + Hg$$

Alkylation, acetylation, silylation and phosphonylation have been reported:

$$Hg[C(CF_3)_2CN]_2 + CH_3I \longrightarrow 2\ CH_3C(CF_3)_2CN + HgI_2 \qquad (\text{ref. } 32)$$



$$CF_3\underset{\overset{\|}{O}}{C}CF_2HgO_2CCF_3 \xrightarrow{2\ CH_3COCl} CF_2{=}\underset{CF_3}{\underset{|}{C}}O_2CCH_3 \qquad (\text{ref. } 57)$$



$$CF_3\underset{\overset{\|}{O}}{C}CF_2HgCl + Me_3SiCl \xrightarrow{60\text{-}70^\circ} CF_2{=}\underset{CF_3}{\underset{|}{C}}\text{-}OSiMe_3 \qquad (\text{ref. } 57)$$

$$R\overset{\overset{O}{\|}}{C}CH_2HgCl + P(OMe)_3 \longrightarrow (MeO)_2P(O)(O\underset{R}{\underset{|}{C}}{=}CH_2) \qquad (\text{ref. } 58)$$

(R = Me_3C, mesityl)

Transition metal-catalyzed conversions of organomercurials are growing in importance. A number of new examples were reported last year. Hydrogenolysis of phenylmercuric acetate could be effected using a homogeneous rhodium(I) catalyst (59):

$$PhHgOAc + H_2 \xrightarrow[30\text{-}50\ \text{psig}]{(Ph_3P)_3RhCl,\ 25^\circ} \underset{(85\%)}{C_6H_6} + \underset{(82\%)}{Hg} + HOAc$$

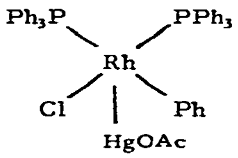
Other examples are shown in Table 2. A 1:1 reaction of $(Ph_3P)_3RhCl$ and phenylmercuric acetate gave complex 3. This complex very likely is the active intermediate in the catalytic reaction since it reacts with hydrogen to give the same products. Complex 3 was found to be a hydroformylation catalyst, but it did not catalyze the carbonylation of methanol.

Table 2. Hydrogenation of Arylmercury Compounds (ref. 59).

$$Y\text{-}C_6H_4HgX \xrightarrow[\text{Solvent}]{H_2,\ \text{Rh Catalyst}} Y\text{-}C_6H_5 + Hg + HX$$

X	Y	Solvent	Yield of $Y\text{-}C_6H_5$ [a]
OAc	H	CH_3OH	85
Cl	H	CH_3OH	73
$OOCCF_3$	H	CH_3OH	98
NO_3	H	CH_3COOH	40
OAc	H	CH_2Cl_2	70
Br	CH_3	$C_2H_5OOCCH_3$	80
OAc	HgOAc	CH_3OH	61 (Y=H)
OAc	COOH	CH_3CH	20

(a) based on arylmercury salt



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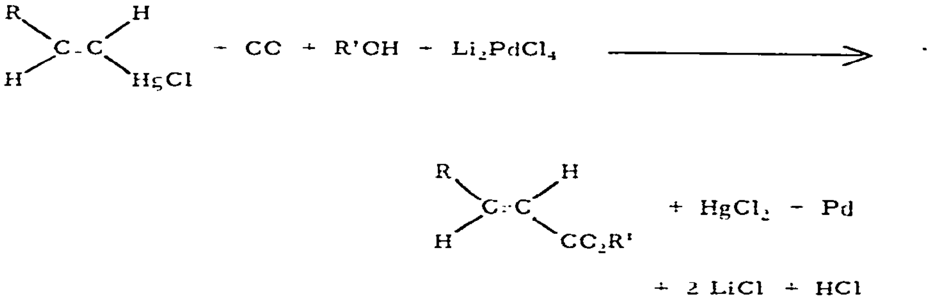
The carbonylation of phenylmercuric acetate to give methyl benzoate, metallic mercury and acetic acid was effected in 88% yield using 100 psig CO in the presence of $(Ph_3P)_3RhCl$ at 85° (59). Vinylmercurials (obtained from vinylboranes by reaction with mercuric acetate) were carbonylated in the presence of Li$_2$PdCl$_4$ to give α, β-unsaturated carboxylic acids and esters (60):



Examples of such reactions are shown in Table 3. A more useful system was one in which only catalytic quantities of PdCl$_2$ or palladium on charcoal were employed in the presence of stoichiometric amounts of cupric chloride.

Table 3. Preparation of α, β-Unsaturated Esters by Li$_2$PdCl$_4$-Mediated Carbonylation of Vinylmercury Compounds (ref. 60).

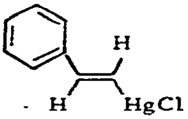
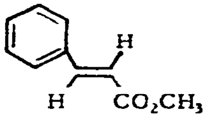
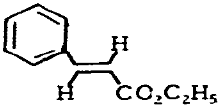
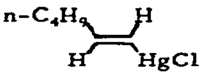
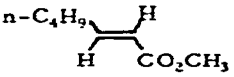
Vinylmercuric chloride	Carboxylic ester	% yield
		100
		99
		98

Table 3. continued

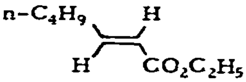
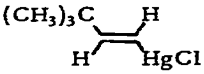
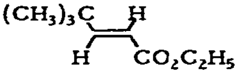
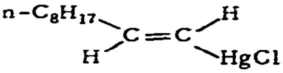
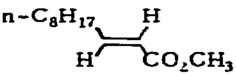
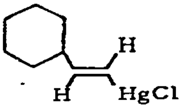
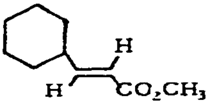
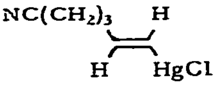
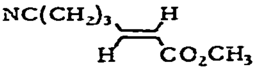
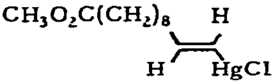
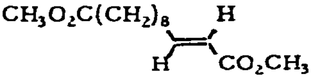
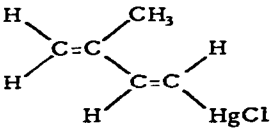
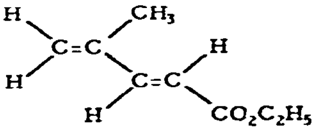
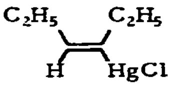
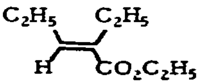
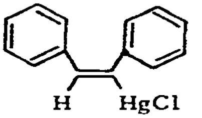
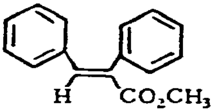
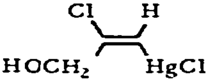
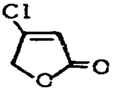
		93
		90
		98
		96
		98
		98
		93
		85

Table 3, continued

		99
		96

(The latter served to reoxidize the palladium metal formed in the process to Pd(II)). α, β -Unsaturated carboxylic acids were prepared similarly in aqueous organic medium (Table 4). Here also a catalytic process which was carried out in the presence of a stoichiometric quantity of $CuCl_2$ was developed:

Table 4. Preparation of α, β-Unsaturated Carboxylic Acids by Li_2PdCl_4-Mediated Carbonylation of Vinylmercury Compounds (ref. 60).

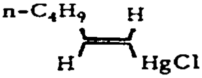
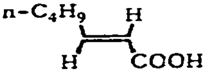
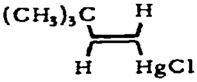
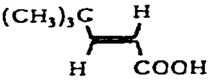
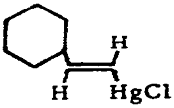
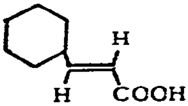
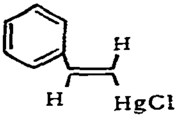
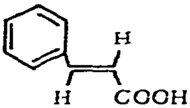
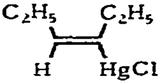
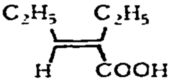
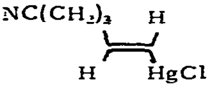
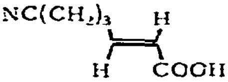
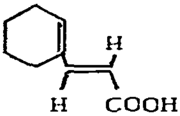
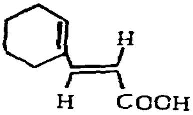
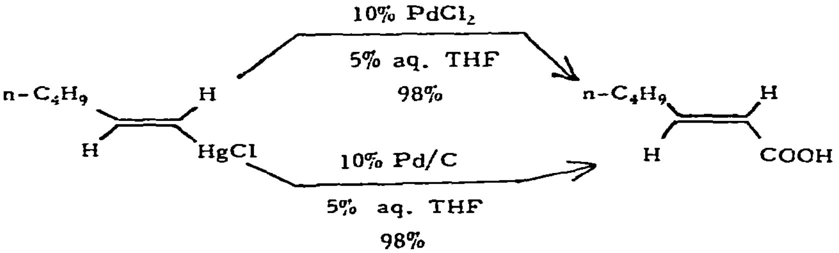
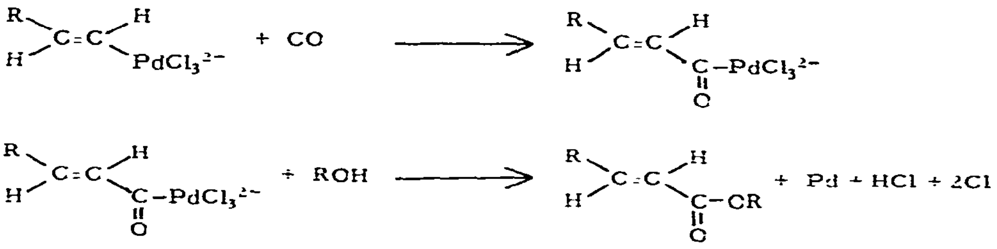
Vinylmercuric chloride	% Aqueous THF	Carboxylic acid	% yield
	5 2		98 99
	5		98
	5 2 1 0.5		65 82 90 77

Table 4. Continued

	5 1		80 30
	5 2		85 60
	5 2		72 65
	5 2 1		45 72 57

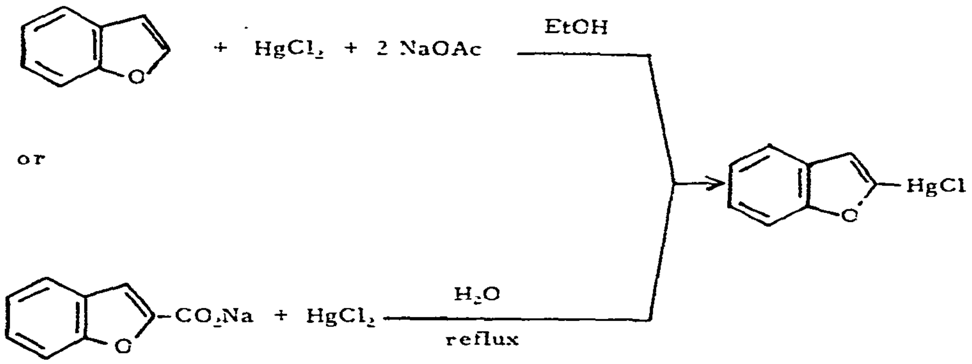


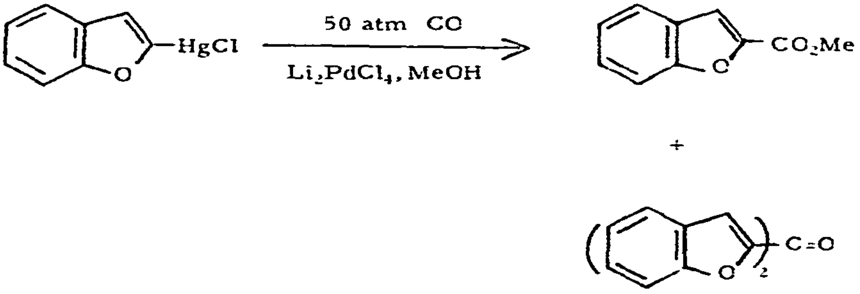
The mechanism for these carbonylations which was suggested is shown below.



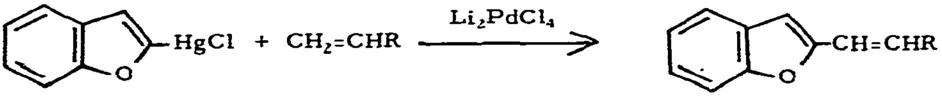
$Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl$

A Japanese group carbonylated 2-benzofurylmercuric chloride (61):

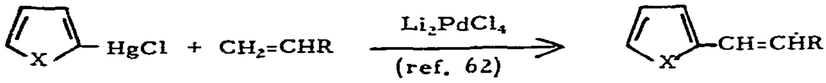




Olefin addition reactions also were studied (61):



(R = Ph, CN, CO_2Et)



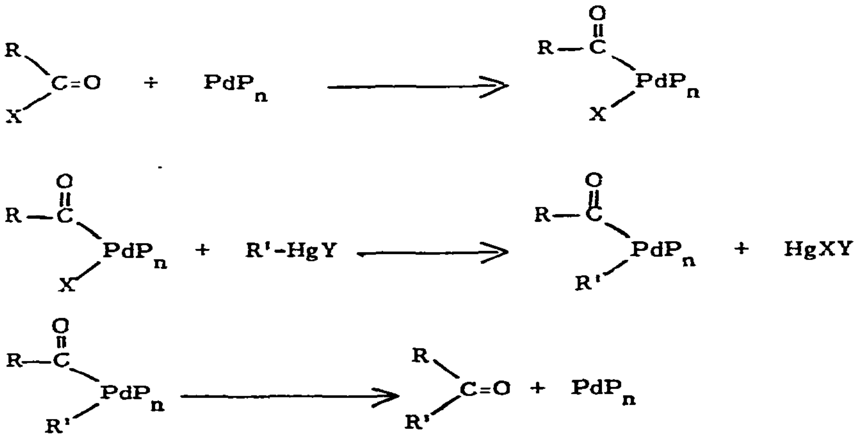
(X = O, S) (R = Ph, CHO, etc.)

Thirteen furylalkenes and six thienylalkenes were prepared in this manner (62).

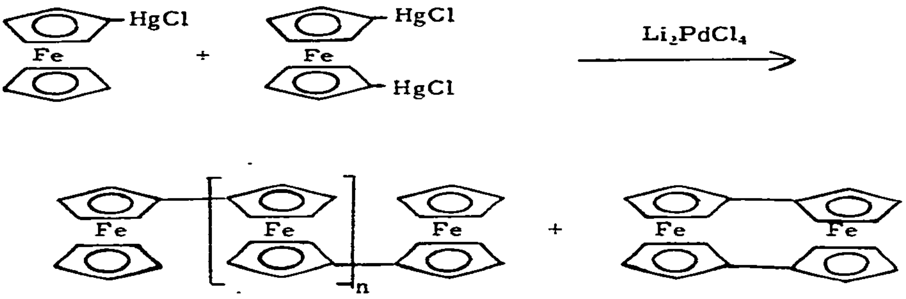
The reaction of organomercurials with acid halides has been found to be catalyzed by tetrakis(triphenylphosphine)palladium in HMPA (63):

$$RC(O)Br + R'HgY \xrightarrow[60^\circ]{(Ph_3P)_4Pd \text{ in HMPA}} RC(O)R' + HgXY$$

The yields are variable but in many cases were preparatively useful (Table 5). The following mechanism was proposed:



The $PdCl_2$-induced coupling of mixtures of ferrocenylmercuric chloride and 1,1'-bis(chloromercuri)ferrocene gave 1,1'-oligomeric ferrocenes (64):



(n = 0-4)

An interesting heterocyclic synthesis has employed the reaction of a cyclic thiourea with $Hg(C{\equiv}CPh)_2$ and an aryl isothiocyanate (65):

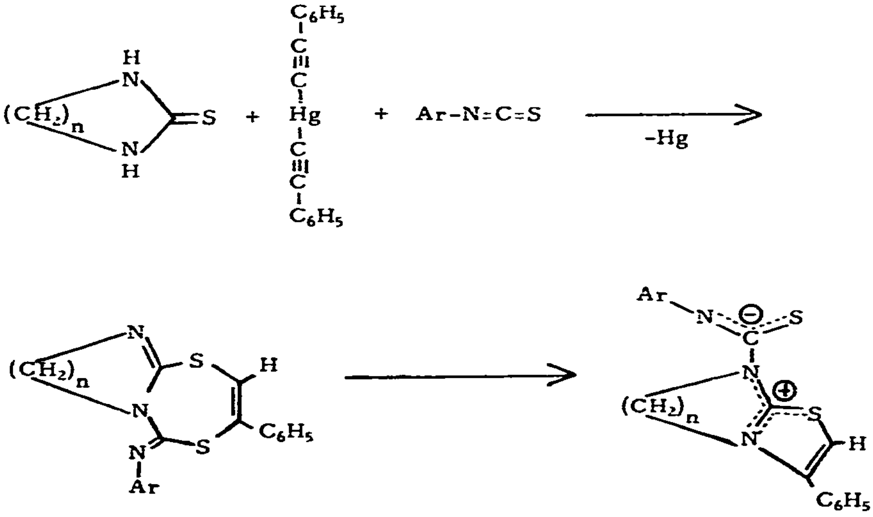


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Table 5. $(Ph_3P)_4Pd$-Catalyzed Reaction of Organomercury Compounds with Acyl Halides (ref. 63).

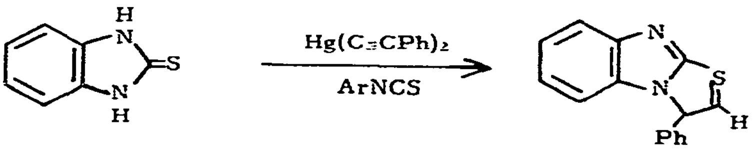
RC(O)Br	R'-HgY		$Pd(PPh_3)_4$	Time	Temp.	Yield	
R	R'	Y	mmol	hr	°C	R-CO-R' %	R'-R' %
Ph	Et	Et	0.01	0.5	60	$77^{b)}$	
Ph	Et	Et	0.01	2	50	$75^{b)}$	
Ph	Et	Et	0.05	0.5	60	$86^{b)}$	
Ph	Et	Et	-	24	60	0	
Ph	Et	Cl	0.01	2	60	$2^{b)}$	
Ph	Ph	Ph	0.005	0.5	60	$64^{c)}$	$12^{c)}$
Ph	Ph	Ph	0.01	0.5	60	$68^{c)}$	$20^{c)}$
Ph	Ph	Cl	0.005	0.5	60	trace	trace
Me	Ph	Ph	0.005	0.5	60	$66^{c)}$	$30^{c)}$
n-Bu	Et	Et	0.04	12	0	$34^{b)}$	

a) HMPA : 1 ml, yield determined by glc.

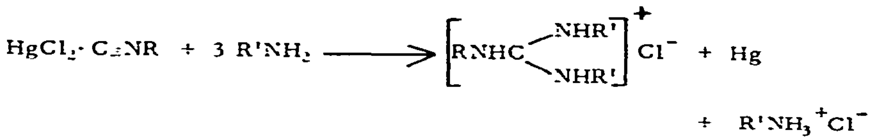
b) yield based on acyl halides used.

c) yield based on organomercury used.

If the nitrogen atoms of the cyclic thiazole intermediate are not sufficiently basic, the rearrangement to the zwitterionic structure (4) does not take place, e.g.:



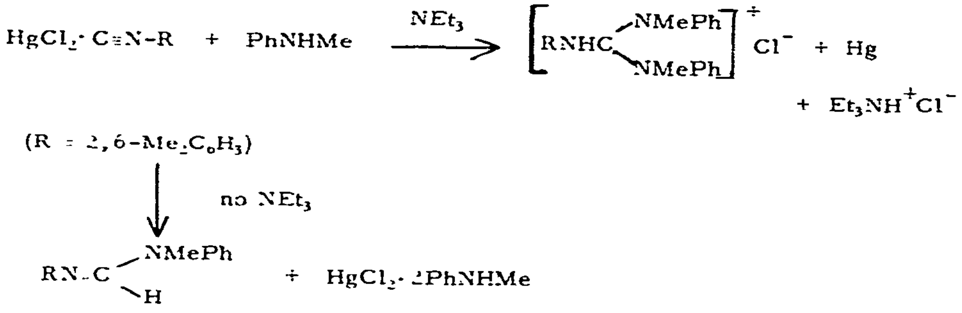
Japanese workers have studied the reactions of isonitrile complexes of mercuric chloride with amines (66):



$$HgCl_2\cdot C{\equiv}NR + 3\,R'NH_2 \longrightarrow \left[RNHC\begin{smallmatrix}NHR'\\NHR'\end{smallmatrix}\right]^+ Cl^- + Hg + R'NH_3{}^+Cl^-$$

($R = Me_3C$, $PhCH_2$, Ph, $2,6\text{-}Me_2C_6H_3$;

$R' = n\text{-}Bu$, Ph, $\underline{c}\text{-}C_6H_{11}$, $H_2NCH_2CH_2$)



$$HgCl_2\cdot C{\equiv}N\text{-}R + PhNHMe \xrightarrow{NEt_3} \left[RNHC\begin{smallmatrix}NMePh\\NMePh\end{smallmatrix}\right]^+ Cl^- + Hg + Et_3NH^+Cl^-$$

($R = 2,6\text{-}Me_2C_6H_3$)

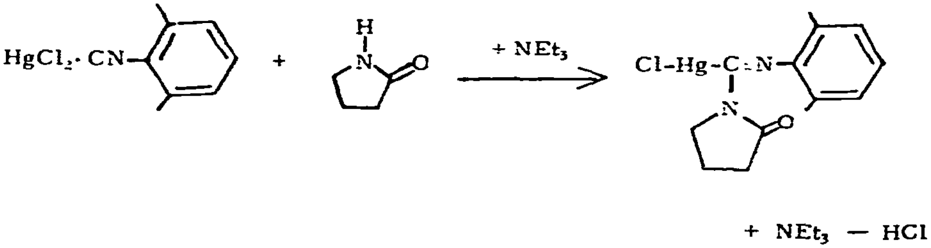
$$\downarrow \text{no } NEt_3$$

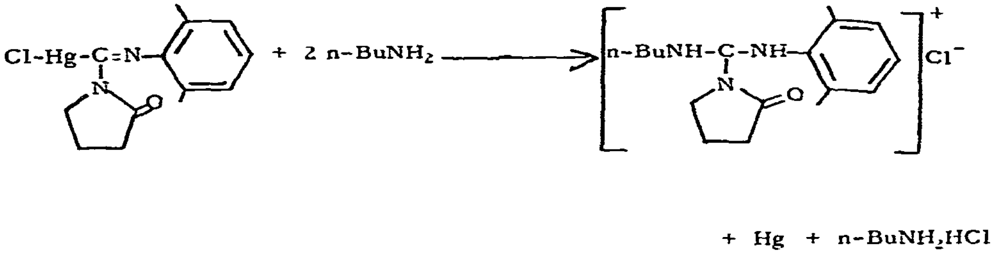
$$RN{=}C\begin{smallmatrix}NMePh\\H\end{smallmatrix} + HgCl_2\cdot 2PhNHMe$$

$$HgCl_2\cdot C{\equiv}N\text{-}R + n\text{-}BuNH_2 \xrightarrow{NEt_3} RN{=}C{=}NBu + Hg + Et_3NH^+Cl^-$$

($R = Me_3C$, $2,6\text{-}Me_2C_6H_3$)

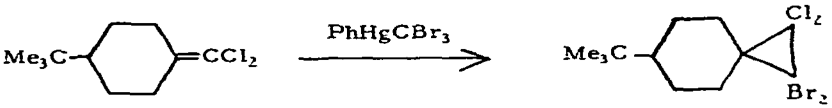
In the case of pyrrolidone, an intermediate organomercurial was isolated:



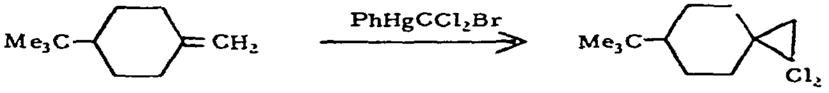


C. Halomethyl-Mercury Compounds

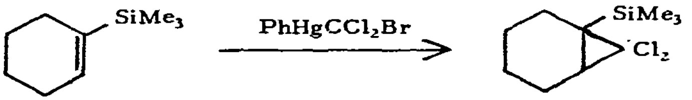
The phenyl(trihalomethyl)mercurials are the most-used of the halomethyl-mercury compounds and we note a number of new examples of their application in the synthesis of dihalocyclopropanes:



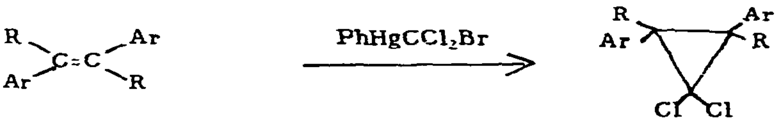
(ref. 67)



(ref. 67)

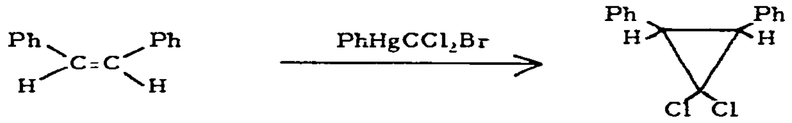


(ref. 68)

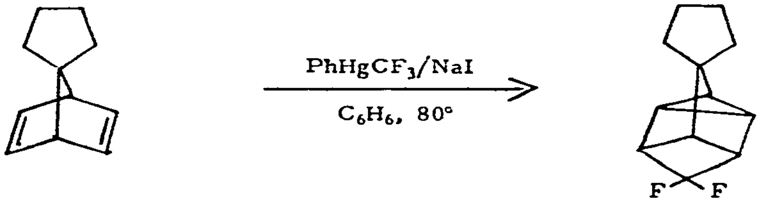


(ref. 69)

R	Ar	% Yield
H	Ph	86
H	4-MeOC$_6$H$_4$	52
Et	4-MeOC$_6$H$_4$	59
Et	4-AcOC$_6$H$_4$	72

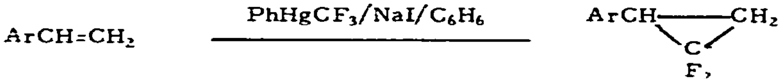


(ref. 69)



(100%)

(ref. 70)

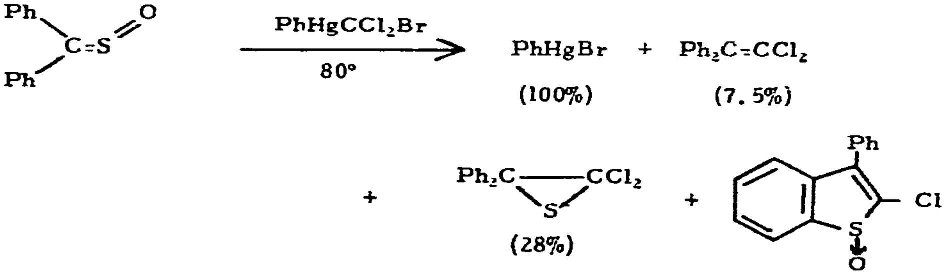


(Ar = p-MeO, p-Me, H,
m-Cl, m-O$_2$N)

(~ 70%)

(ref. 71)

The reactions of PhHgCCl$_2$Br and of PhHgCCl$_2$Br/NaI with an episulfoxide have been reported (71a):

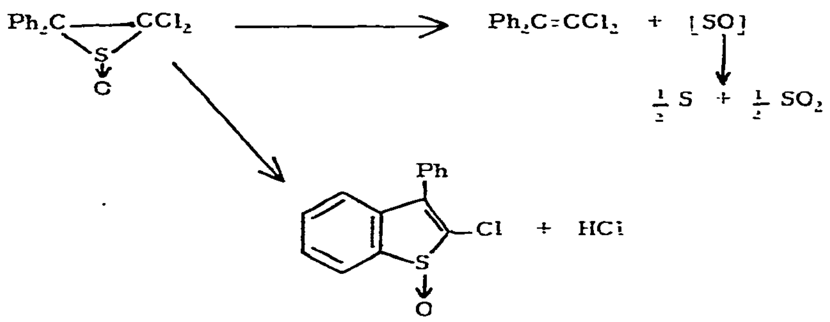


(100%) (7.5%)

(28%)

(5%)

All of these products are derivable from the initial CCl_2 adduct:



The same products were obtained when the $PhHgCCl_2Br/NaI$ reagent (in DME at 25°) was used.

Full details have been published concerning the preparation and reactivity of reagents of type PhHgCXYI (X, Y = Cl, Cl; Cl, Br; Br, Br) (72). Because of the extreme lability of these compounds, it was necessary to carry out their preparation at -70° and to perform all reaction and work-up steps as rapidly as possible. These reagents are stable as the dry solids at 0°, but decompose in solution. They are extremely reactive dihalocarbene transfer agents, as the comparison with analogous PhHgCXYBr reagents shows (Table 6). In particular, these reagents find useful synthetic

Table 6. Times Required for Decomposition in Benzene Solution in the Presence of Cyclohexene at Room Temperature (ref. 72).

Compound	X = Br	X = I
$PhHgCCl_2X$	18 days	24 hr
PhHgCClBrX	16 days	4 days
$PhHgCBr_2X$	15 days	7 days

(Continued on p. 210)

Table 7. Divalent Carbon Transfer Reactions of Phenyl(iododihalomethyl)mercury Compounds

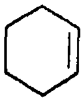
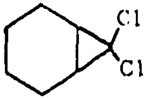
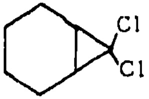
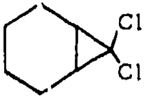
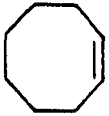
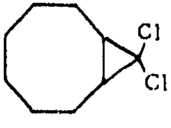
Mercury reagent[a] (mmol)	Carbenophile (mmol)		Ml of benzene	Reaction time	Reaction temp. °C	Product (% yield)		PhHgI, % yield
PhHgCCl$_2$I (10.5)		(30)	15	24 hr	25		(89)	92
PhHgCCl$_2$I (10)		(30)	25	<1 min	80		(85)	94
PhHgCCl$_2$I (7.5)		(30)	15	8 days	0		(71)	80
PhHgCCl$_2$I (7.3)		(30)	15	24 hr	25		(93)	93

Table 7, continued

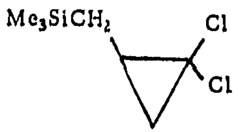
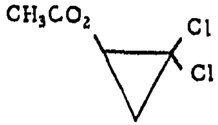
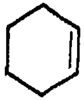
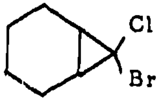
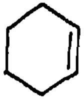
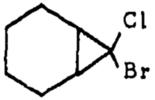
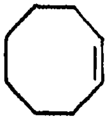
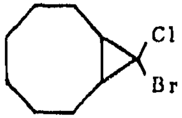
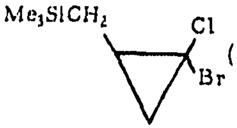
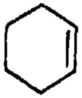
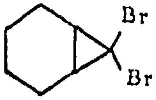
PhHgCCl$_2$I (9.8)	Me$_3$SiCH$_2$CH=CH$_2$	(30)	15	24 hr	25		(95)	88
PhHgCCl$_2$I (10)	CH$_3$CO$_2$CH=CH$_2$	(30)	15	24 hr	25		(38)	72
PhHgCCl$_2$I (7.1)	Et$_3$SiH	(30)	15	24 hr	25	Et$_3$SiCCl$_2$H	(83)	82
PhHgCClBrI (10)		(30)	20	4 days	25		(75)^b	80
PhHgCClBrI (10)		(30)	50	< 10 min	80		(81)^b	82

Table 7. continued

PhHgCClBrI (10)		(30)	20	4 days	25		$(83)^b$	87
PhHgCClBrI (10)	$Me_3SiCH_2CH{=}CH_2$	(30)	20	4 days	25		$(78)^b$	80
PhHgCClBrI (10)	Et_3SiH	(30)	20	4 days	25	$Et_3SiCHBrCl$	(60)	84
$PhHgCBr_2I$ (10.4)		(30)	20	7 days	25		(65)	70

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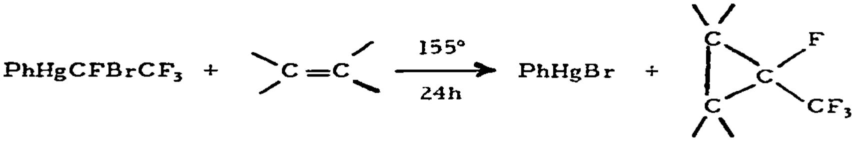
a) Number of millimoles of active reagent in sample used (usually 70-90% purity).

b) Mixture of isomers.

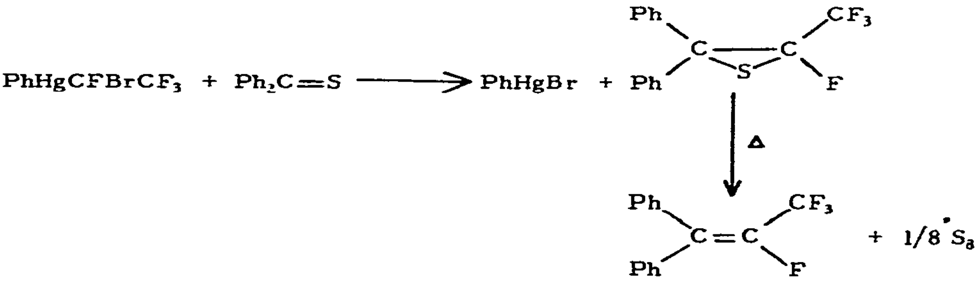
application as room temperature sources of dihalocarbenes. Some dihalocyclopropanations effected with them are listed in Table 7.

Phenyl(1-bromo-1, 2, 2, 2-tetrafluoroethyl)mercury, $PhHgCBrFCF_3$, is an excellent source of tetrafluoroethylidene, CF_3CF (73):

$$PhHgCl + CF_3CHFBr + NaOCH_3 \text{ (in } CH_3OH) \xrightarrow{\text{THF, -35°}} PhHgCFBrCF_3 + NaCl + CH_3OH$$



At 155°, excellent yields of CF_3CF transfer products were obtained (Table 8). In the reaction of this mercurial reagent with thiobenzophenone, the initially formed product was unstable, undergoing sulfur extrusion under the reaction conditions:



Similar behavior was found in the reaction of thiobenzophenone with $PhHgCFBrCO_2Et$; here the isolated product was $Ph_2C{=}CFCO_2Et$ rather than the expected thiirane. The reaction of this organomercury reagent with thiofluorenone gave 5 (73).

(Continued on p. 213)

Table 8. CF_3CF Transfer Reactions of $PhHgCFBrCF_3$ (ref. 73)

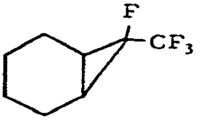
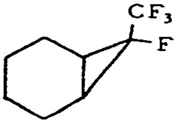
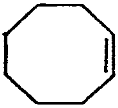
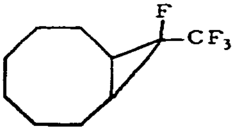
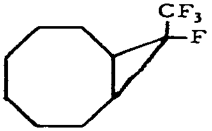
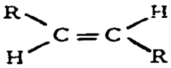
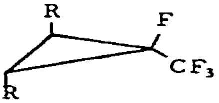
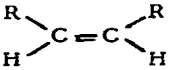
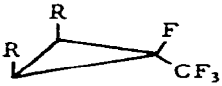
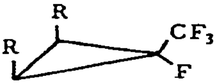
Olefin	Yield of PhHgBr (%)	Cyclopropane product^b	Yield (%)
	87	 + 	(3.6 parts) 87 (1 part)
	96	 	(3.4 parts) 98 (1 part)
 (R = n-Pr)	92		80
 (R = n-Pr)	83	 + 	(5.8 parts) 77 (1 part)

Table 8. continued

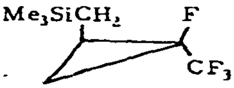
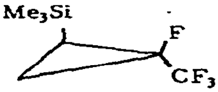
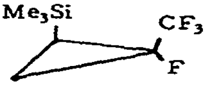
$n\text{-}C_5H_{11}{=}CH_2$[c]	80	 + 	(1.9 parts) 70 (1 part)
$Me_3SiCH_2CH{=}CH_2$[d]	99	 + 	(1.8 parts) 93 (1 part)
$Me_3SiCH{=}CH_2$[e]	60	 + 	(3.1 part) 16 (1 part)
Et_3SiH	61	$Et_3SiCHFCF_3$	53

Table 8. continued

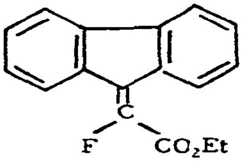
a) Reactions at 155° for 24 h in a sealed tube, olefin to mercurial ratio 3/1, benzene diluent, unless otherwise noted.

b) Isomer assignments are tentative except in the case of the cyclooctene reaction product.

c) 72 h reaction time.

d) Olefin (10 ml) used as solvent.

e) 48 h reaction time.



5

The mercurial $PhHgCFBrCF_2OEt$ was prepared in similar manner, but it was not a source of transferrable $EtOCF_2CF$ (73).

$$PhHgCl + CHBrFCF_2OC_2H_5 + Me_3COK/Me_3COH \longrightarrow KCl + 2\ Me_3COH + PhHgCFBrCF_2OC_2H_5$$

The ultraviolet photolysis of trichloromethylmercury compounds has been studied in the solid phase (74) and in the gas phase and in solution (75) by Nefedov and his coworkers. The volatile products of solid CCl_3HgCl and $(CCl_3)_2Hg$ photolysis consisted of 80-90% CCl_4 and C_2Cl_6, indicating the photodissociation process

$$RHgCCl_3 \xrightarrow{h\nu} RHg\cdot + Cl_3C\cdot$$

(rather than extrusion of CCl_2)

followed by the secondary processes

$$Cl_3C\cdot + RHgCCl_3 \longrightarrow CCl_4 + RHgCCl_2\cdot$$

and

$$2\ Cl_3C\cdot \longrightarrow Cl_3C\text{-}CCl_3$$

Tetrachloroethylene also was formed. The authors suggested a radical pathway for its production:

$$ClHgCCl_2\cdot \longrightarrow \tfrac{1}{2}\ Cl_2C{=}CCl_2 + ClHg\cdot$$

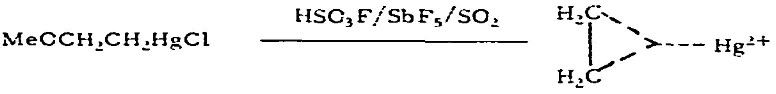
$$CCl_3HgCCl_2\cdot \longrightarrow Cl_2C{=}CCl_2 + ClHg\cdot$$

Phenyl(trichloromethyl)mercury was much more stable toward solid phase photolysis due to inhibition by accumulated colored polymeric products on the surface. In the gas phase at 80° and in 1,2-dimethoxyethane solution at 18°, the photolysis of $Hg(CCl_3)_2$ gave hexachloroethane and chloroform, respectively, as main products. Thus under these conditions photodissociation also produces the trichloromethyl radical.

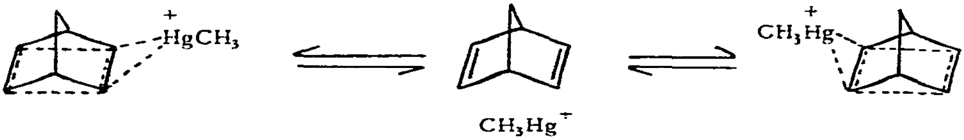
4. MERCURATION OF UNSATURATED COMPOUNDS

A. Olefins

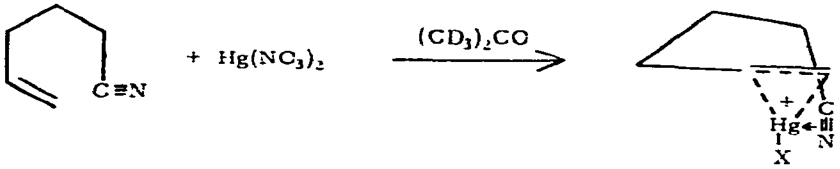
Olah and Yu (76) reported further NMR studies of mercurinium ions, the species which many (but not all) believe to be intermediates in the olefin solvomercuration reaction. The observed ^{13}C NMR parameters (δ_C and J(^{13}C–^{1}H) of the ethylenemercurinium ion led to a bonding picture in which σ-donation from the olefin to the Hg^{2+} ion predominated, with a resulting decrease in electron density at the olefinic carbon atoms. The ethylenemercurinium ion was formed as follows:



Similar studies were made of the 1:1 norbornadiene- and 1,5-cyclooctadiene-mercurinium ions using CH$_3$HgC$_3$SF in liquid SO$_2$ at -78° as the olefin mercurating agent. The norbornadiene-derived mercurinium ion was pictured in terms of the following equilibrium:



Observation of a mercurinium ion by NMR also was reported by French workers (77):

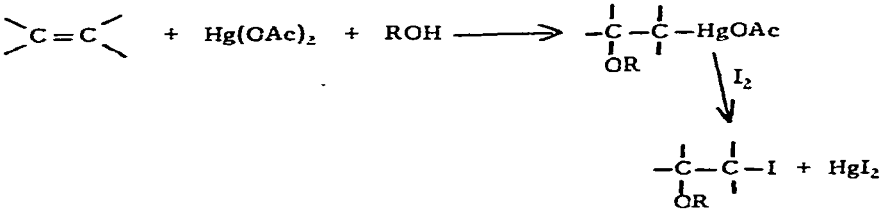


6

The remarkable stability of the observed species, presumably 6, was attributed to intramolecular π-type coordination of the C≡N group to the mercury ion.

Olefin solvomercuration, often followed by reductive or oxidative cleavage of the mercury moiety, has become an important process in organic synthesis. We present some of the results of the past year, but must emphasize that our coverage is by no means complete. Now that the solvomercuration reaction has become an accepted synthetic tool, largely through the efforts of H.C. Brown and his coworkers, many examples of its application are tucked away in long papers on organic synthesis and never mentioned in the title or abstract. Some of these examples we will have missed.

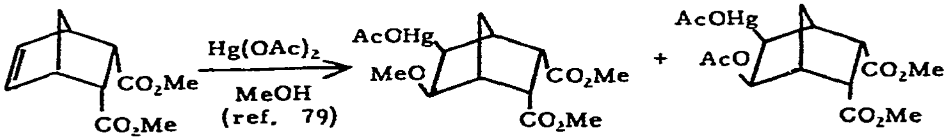
French workers have prepared a number of β-iodo-ethers in good yield by an olefin alkoxymercuration-iodinolysis sequence (78):

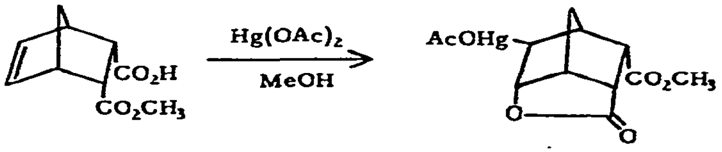


$$>C=C< + Hg(OAc)_2 + ROH \longrightarrow -\overset{|}{\underset{OR}{C}}-\overset{|}{\underset{|}{C}}-HgOAc \xrightarrow{I_2} -\overset{|}{\underset{OR}{C}}-\overset{|}{\underset{|}{C}}-I + HgI_2$$

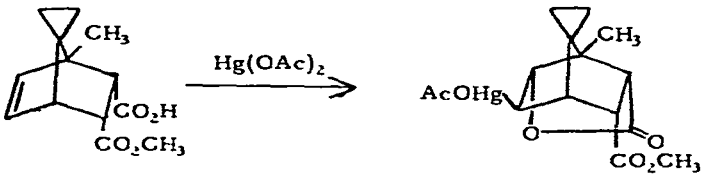
The results are given in Table 9.

Other reported olefin solvomercuration reactions include the following.

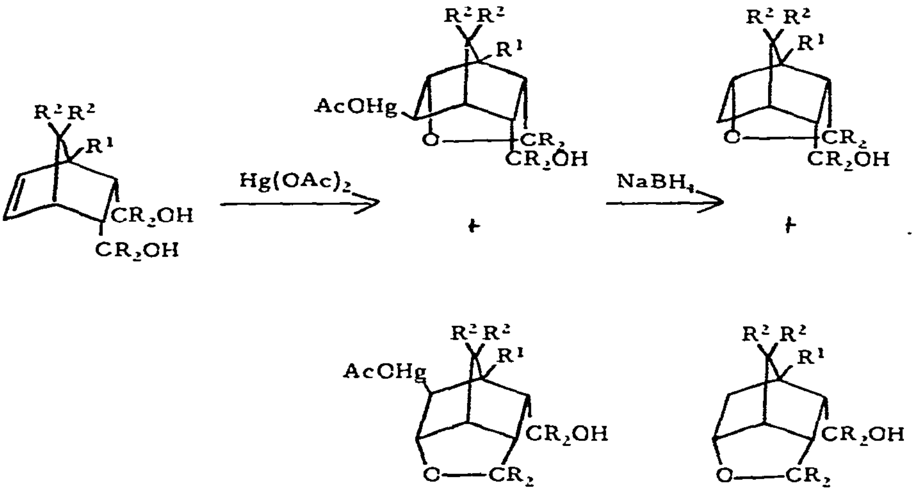




(ref. 79)

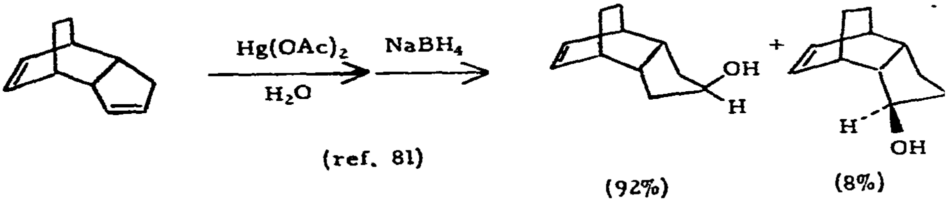


(ref. 79)



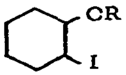
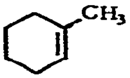
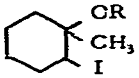
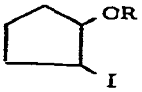
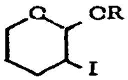
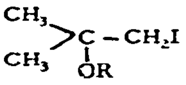
	R	R^1	R^2, R^2
a	D	CH_3	CH_2-CH_2
b	H	CH_3	H, H
c	H	CH_3	CH_3, CH_3
d	H	C_2H_5	H, H
e	H	t-C_4H_9	H, H

(ref. 80)

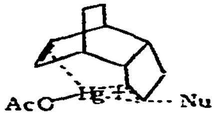


(ref. 81)

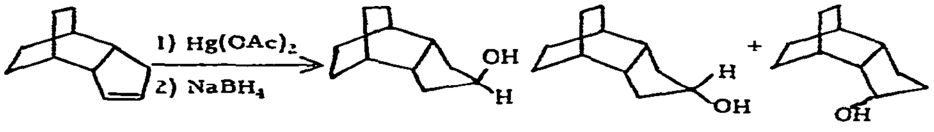
Table 9. Alkoxymercuration-Iododemercuration of Olefins (Ref. 78)

Olefin	Product	Yield, %	
		R = CH_3CO- CH_3- $C_6H_5CH_2-$ $H-$	80-85 95-100 82 90
		R = CH_3- $C_6H_5CH_2-$	85 80
		R = CH_3CO- CH_3- $C_6H_5CH_2-$ $H-$	90 77 65 66
		R = CH_3- $C_6H_5CH_2-$	70 73
$(CH_3)_2C=CH_2$	 $(CH_3)_2C(OR)-CH_2I$	R = CH_3- $C_6H_5CH_2-$	85 73

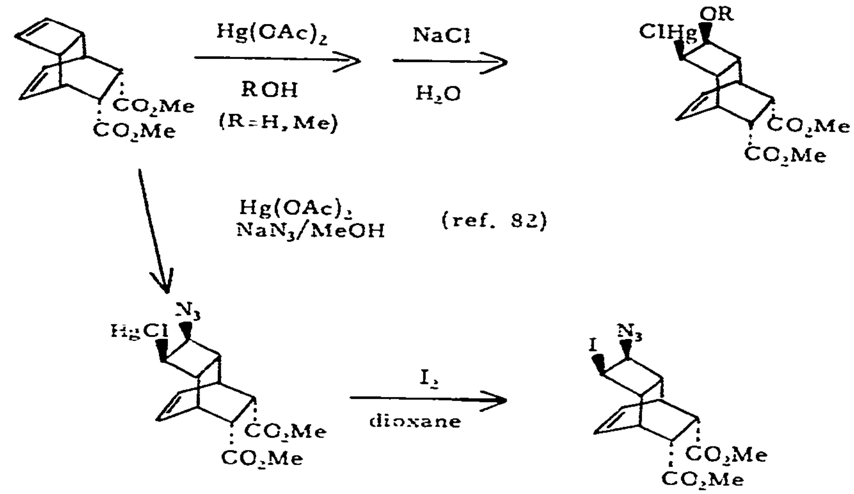
Transition state 7 was suggested for this reaction (81).

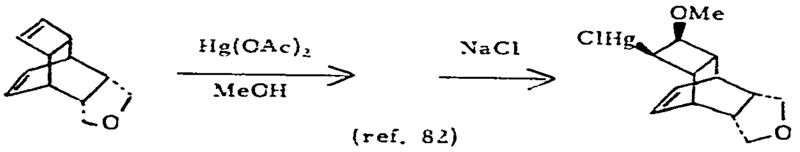


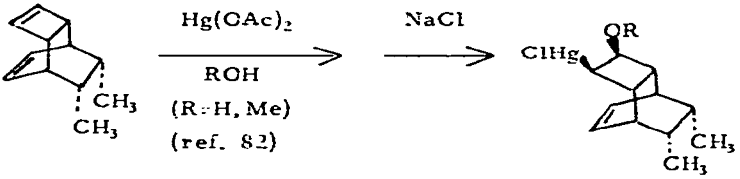
7



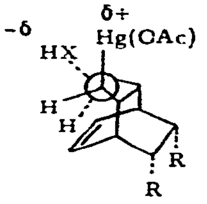
(ref. 81) (43%) (22%) (35%)



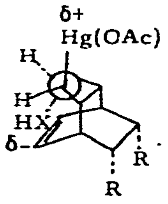




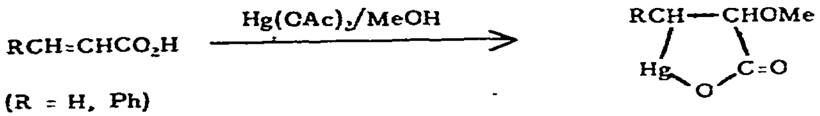
These are the first examples of *syn* addition of mercuric acetate-ROH to a cyclobutene. They were explained in terms of Traylor's twist strain theory (82), with transition state 8 being favored over strained anticoplanar 9.



8

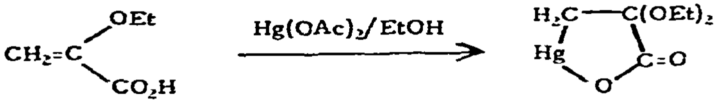


9



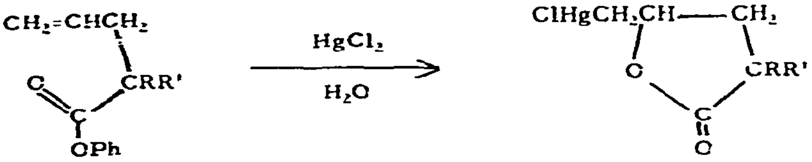
(ref. 83)

(R = H, Ph)



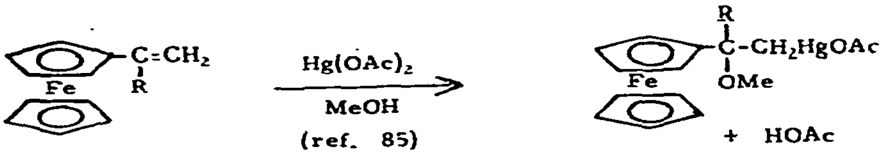
(ref. 83)

Without doubt, the structures claimed by the workers who reported these results are not correct since mercury does not form cyclic compounds in which the -Hg- angle deviates much from 180°. No useful experimental evidence (e.g., solution molecular weights) was given in support of the claimed structures.



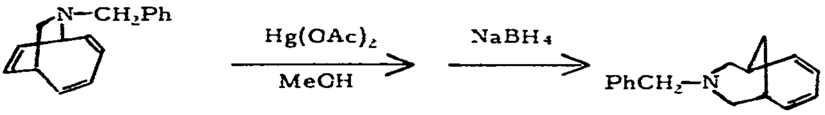
(R = H, R' = H;
R = H, R' = Ph;
R = Ph, R' = Ph)

The second order rate constants for this reaction increased from R,R' = H (1.4×10^{-3} $M^{-1}min^{-1}$) to R = H, R' = Ph (6.3×10^{-3} $M^{-1}min^{-1}$) to R,R' = Ph (120×10^{-3} $M^{-1}min^{-1}$) (84).

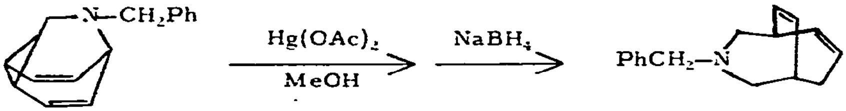


(R = H, Me)

(A kinetic study was carried out).

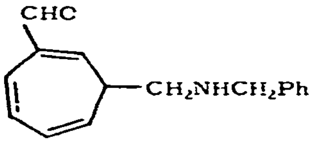


(ref. 86)

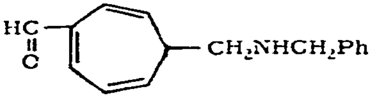


(ref. 86)

In aqueous medium, oxidative demercuration occurred, giving 10 and 11, respectively. Schemes 1 and 2 rationalize these results.

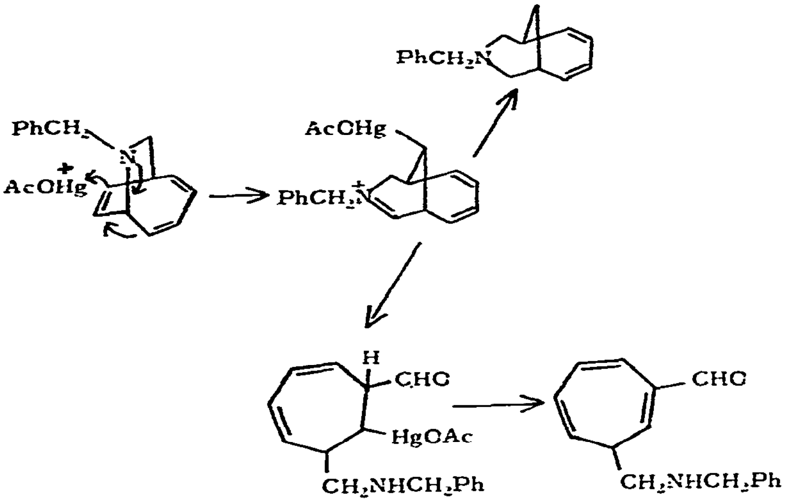


10

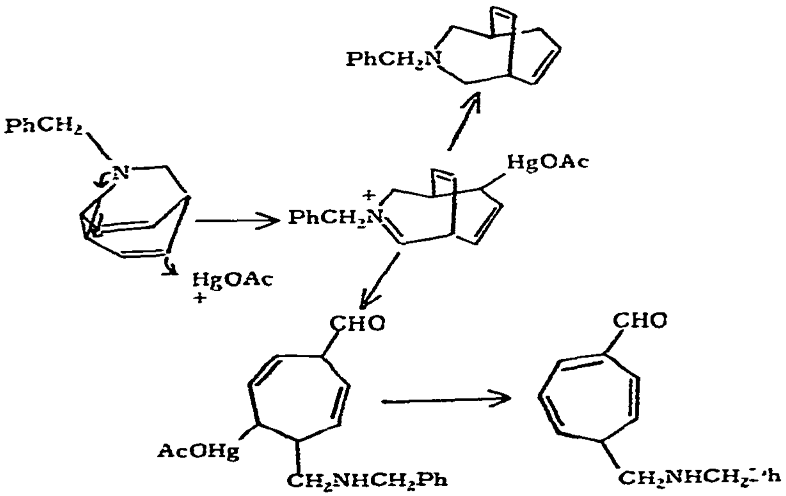


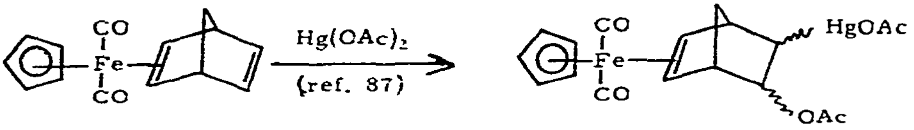
11

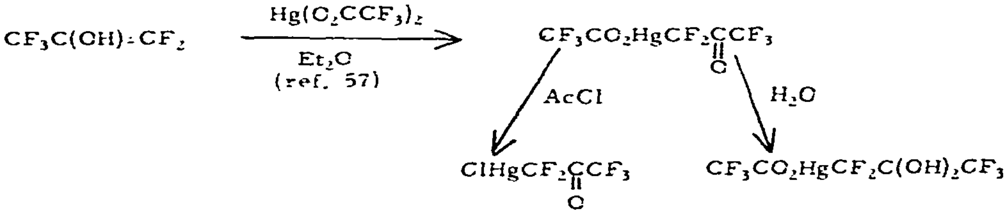
Scheme 1



Scheme 2

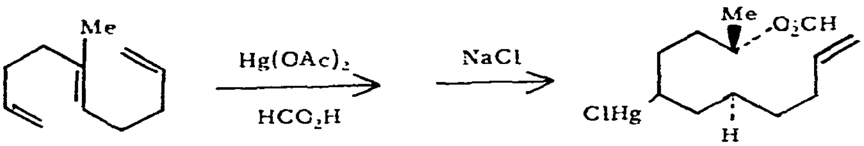




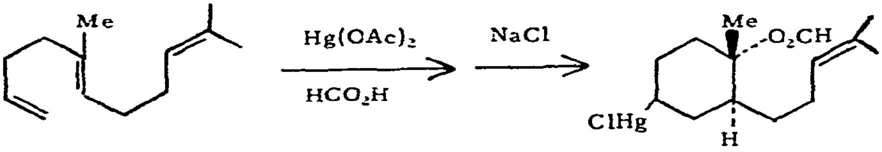


Solvomercuration of unsaturated sugars (88, 89), of piperitone and carvone (90) and of (-)- γ -cadinene (91) has been reported.

Julia has reported more examples of cyclization reactions during olefin mercuration:

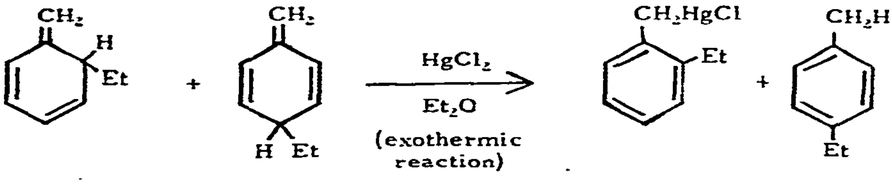


(ref. 92)



(ref. 93)

Of note is the mercuration of a mixture of trienes 12 and 13 (tautomeric o- and p-ethyltoluenes) which results in aromatization (94, 95):



12 13

The trienes 12 and 13 may be prepared by reaction of benzylmagnesium chloride with diethyl sulfate (94) or in situ by reaction of $(PhCH_2)_3SnCl$ with HCl in dioxane in the presence of mercuric chloride. (95).

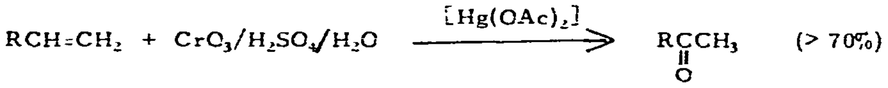
Mercuric trifluoroacetate is superior to mercuric acetate in the peroxymercuration of olefins in that no acyloxymercuration occurs as a competitive side reaction when the former is used (96).

$$>C=C< + Hg(O_2CCF_3)_2 + Me_3COOH \xrightarrow{CH_2Cl_2} >C(OOCMe_3)\overset{|}{\underset{|}{C}}HgO_2CCF_3 + CF_3CO_2H$$

This reaction was applied to a number of olefins: C_2H_4, C_3H_6, styrene, cis- and trans-2-butene, trans-3-hexene, cis- and trans-stilbene, trans-propenylbenzene, cyclohexene, norbornene and isobutylene. The stereochemistry of these addition reactions has been studied using proton NMR spectroscopy (97).

Some other reactions of mercury(II) salts with olefins do not result in formation of stable organomercury products but do involve organomercury intermediates which undergo demercuration, e.g., Hg(II)-

catalyzed rearrangement of Δ^5-steroids to A-homo-B-nor-derivatives (98) and oxidation of terminal and internal olefins. The latter reaction has received more detailed study (99, 100). A useful catalytic terminal olefin-to-methyl ketone oxidation has been developed (101):

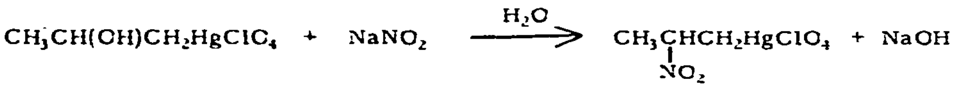


$$RCH{=}CH_2 + CrO_3/H_2SO_4/H_2O \xrightarrow{[Hg(OAc)_2]} R\underset{\underset{O}{\|}}{C}CH_3 \quad (> 70\%)$$

Such oxidations did not proceed so well with 1,2-disubstituted olefins.

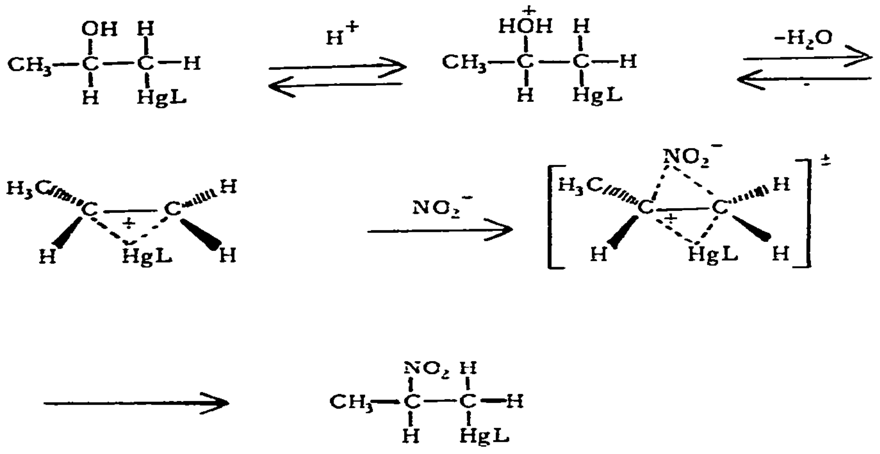
Cationic polymerization of styrene can be initiated with mercuric perchlorate or with phenylmercuric perchlorate (102). Separation of mercury was observed in the case of the former but did not occur with $PhHgClO_4$.

A few studies of the further chemistry of olefin oxymercuration products merit mention, including investigation of hyperconjugative deuterium isotope effects on the redox decomposition of hydroxymercurated 2-butenes in aqueous medium (103) and of the reaction of hydroxymercurated propene with sodium nitrite (104):

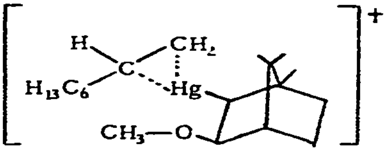


$$CH_3CH(OH)CH_2HgClO_4 + NaNO_2 \xrightarrow{H_2O} CH_3\underset{\underset{NO_2}{|}}{C}HCH_2HgClO_4 + NaOH$$

A detailed study of secondary deuterium isotope effects in this reaction favored the operation of a mercurinium ion mechanism:



The exchange reaction between an olefin and an olefin oxymercuration product has been studied using an optically active oxymercurial in exchange with a racemic olefin. Evidence was obtained that both the optically active oxymercurial and the exchanging olefin are coordinated at mercury in the rate-limiting step (105). A bis-olefin-mercury cation, such as 14 in one example described, appears to be involved as an intermediate.



14

B. Acetylenes

The acetylene function is known to be quite reactive toward mercuric chloride, and some new examples of such chloromercurations have been reported.

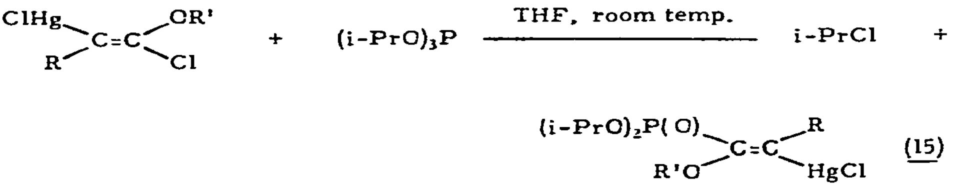
(ref. 106)

$$HC{\equiv}C\text{-}CH{=}CH_2 \xrightarrow[70\text{-}80^\circ]{HgCl_2,\ PhMe} ClHgCH{=}CH\text{-}CH{=}CHCl \qquad \text{(ref. 107)}$$

The structure of the adduct in the first reaction was assigned on the basis of its dipole moment ($\mu = 1.70 \pm 0.09$ D vs. $\mu_{calcd} = 1.56$ D). It is not clear whether the second reaction gave the same or a different product since only the abstract was available and no melting point or other characterizing data were given.

(R = H, Me, Et, i-Pr;
R' = Me, Et, n-Bu)

These vinylic mercurials were unstable at room temperature but could be stored for a few days at -20° (108). They underwent the Arbuzov reaction with triisopropyl phosphite (109).

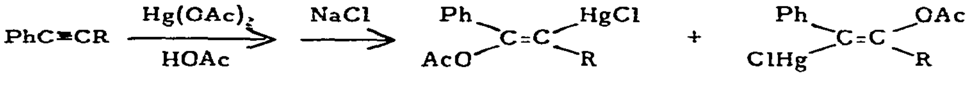


(15)

Compounds of type 15 also can be made in a one-step process (109):

$$(i\text{-}PrO)_3P\cdot HgCl_2 + RC\equiv COR' \longrightarrow \underline{15} + i\text{-}PrCl$$

Acetoxymercuration of alkylphenylacetylenes is not regiospecific but is stereospecific (110):



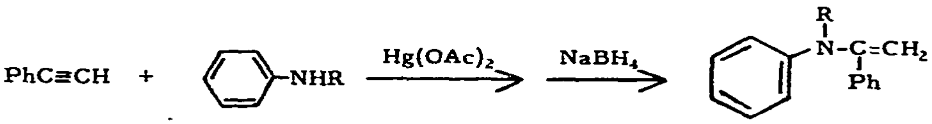
16 17

The 16/17 ratio was a function of the chain length of R:

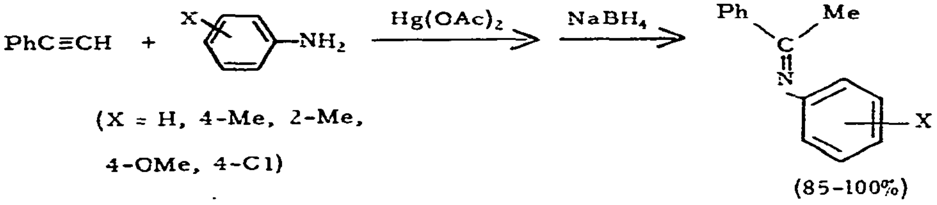
R	16/17
Me	3.0
Et	5.0
n-Pr	11.0
n-Bu	16.5

This was ascribed to the operation of steric effects in OAc^- attack on the intermediate mercurinium ion.

Aminomercuration of phenylacetylene has been used in the synthesis of imines and enamines (111):

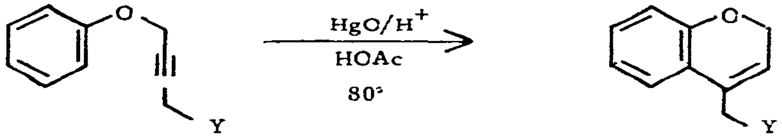


(R = Me, Et, $PhCH_2$)



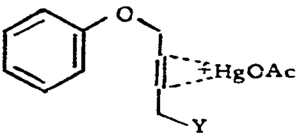
(X = H, 4-Me, 2-Me, 4-OMe, 4-Cl)

Examples of a novel Hg(II)-catalyzed conversion of aryloxybutynes to chromenes have been reported (111a):



(Y = SAr, SO_2Ar)

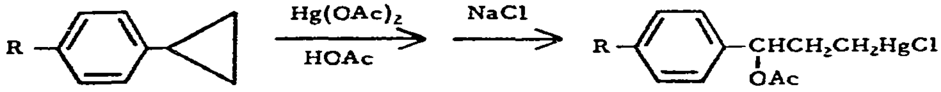
Intramolecular electrophilic attack by a mercurinium ion intermediate, 17a, would serve to explain the formation of the cyclic product.



17a

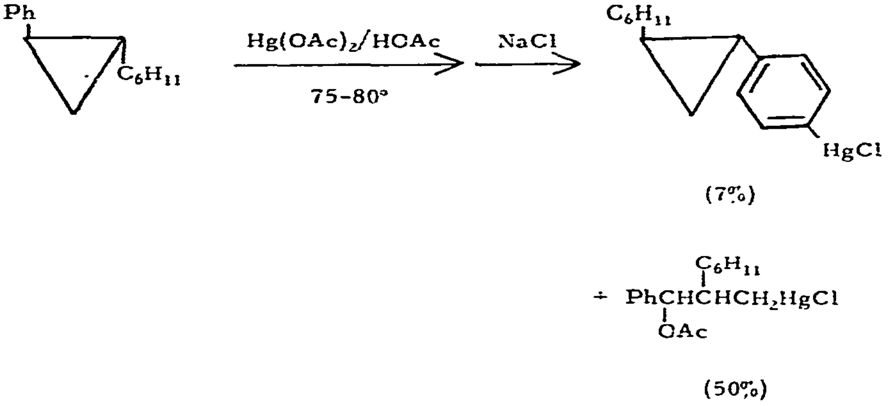
C. Cyclopropanes

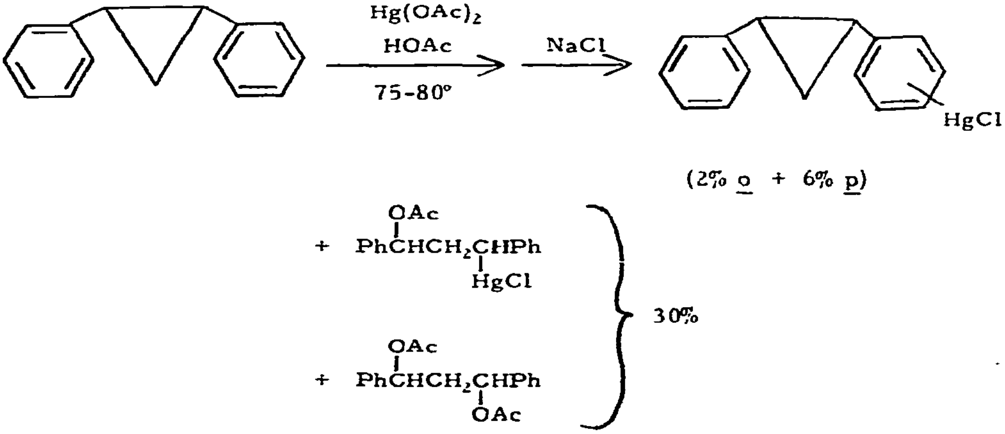
The effect of para substituents on the reaction of mercuric acetate with phenylcyclopropanes has been investigated (112):

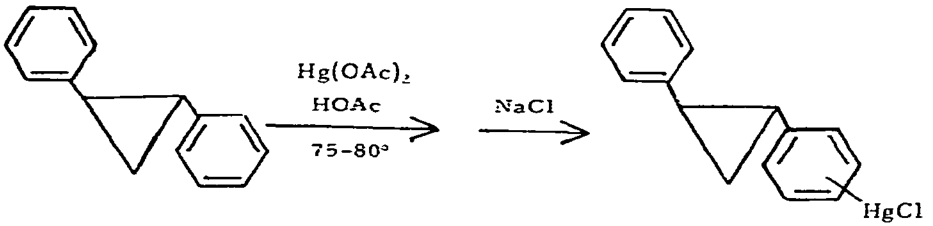


(R = H, Me_3C, Ph, cyclo-C_3H_5)

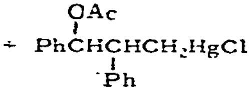
The tert-butyl and particularly the cyclopropyl substituents were found to accelerate the reaction, while the phenyl group retarded it. Also studied was the mercuration of trans-1-phenyl-2-cyclohexylcyclopropane and the stereoisomeric 1,2-di- and 1,2,3-triphenylcyclopropanes (113, 114). Two types of reaction, cleavage of the cyclopropane ring and mercuration of the benzene rings, were encountered:





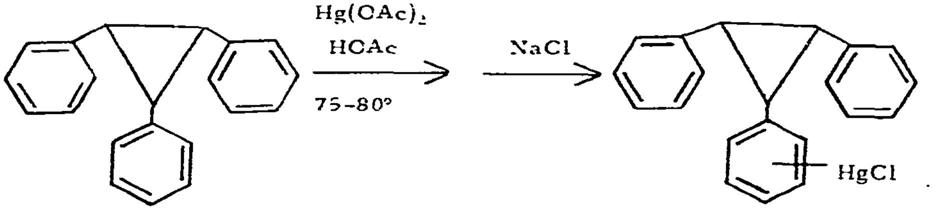


(3.5% o + 21% p)

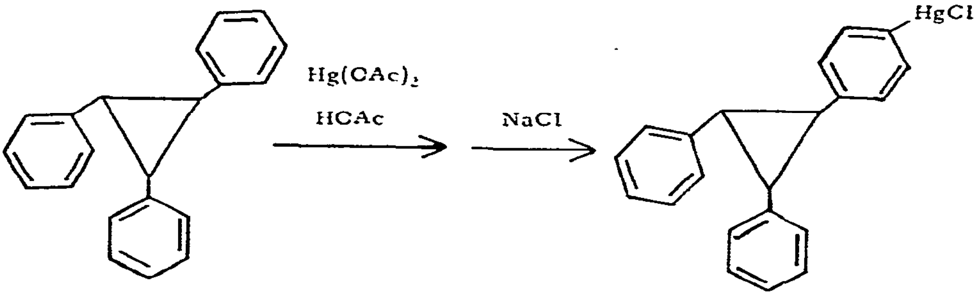


$$+\ \mathrm{Ph\overset{\overset{\displaystyle OAc}{|}}{C}H\underset{\underset{\displaystyle Ph}{|}}{C}HCH_2HgCl}$$

(21%)

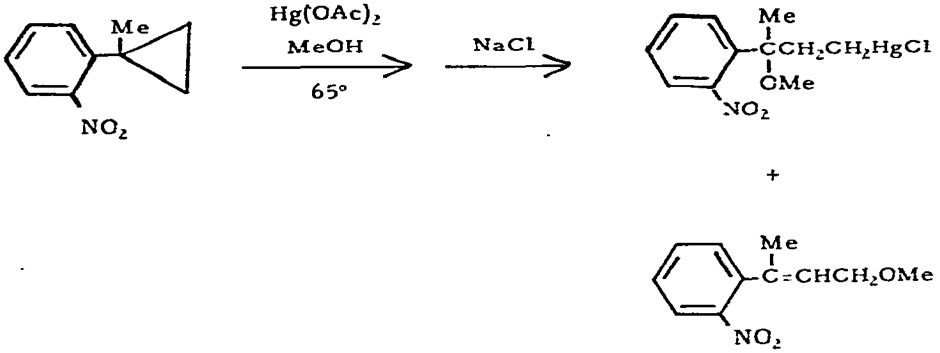


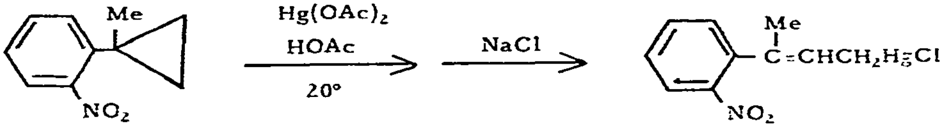
(7% o + 14% p)



(27%)

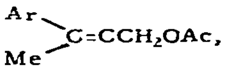
Two types of behavior also were observed in the reaction of mercuric acetate in methanol and in acetic acid with 1-methyl-1-o-nitrophenylcyclopropane: normal ring opening and the formation of allylic organomercurials (115). Mercury-free products derived from the latter were found as well.





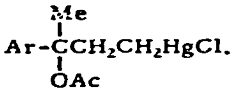
(63%)

An increase in the reaction temperature or the use of perchloric acid as a catalyst in the second reaction resulted in formation of other products as well:



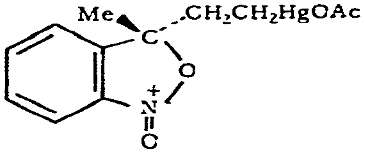
$\begin{matrix}\mathrm{Ar}\\ \mathrm{Me}\end{matrix}\!>\!\mathrm{C{=}CCH_2OAc},$

$\begin{matrix}\mathrm{Ar}\\ \mathrm{Me}\end{matrix}\!>\!\mathrm{CHCH{=}CH_2},$



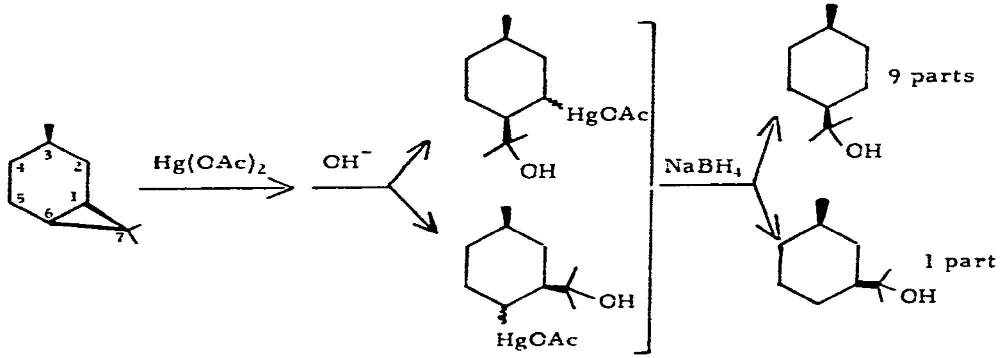
$\mathrm{Ar{-}\overset{\displaystyle Me}{\underset{\displaystyle OAc}{C}}CH_2CH_2HgCl}.$

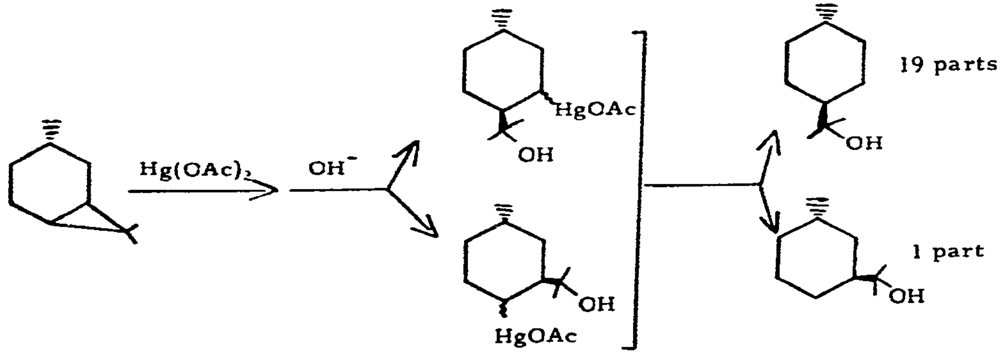
It was suggested that 18 is an intermediate in these reactions, with proton loss giving the allylic mercurial which can undergo demercuration under more forcing conditions.



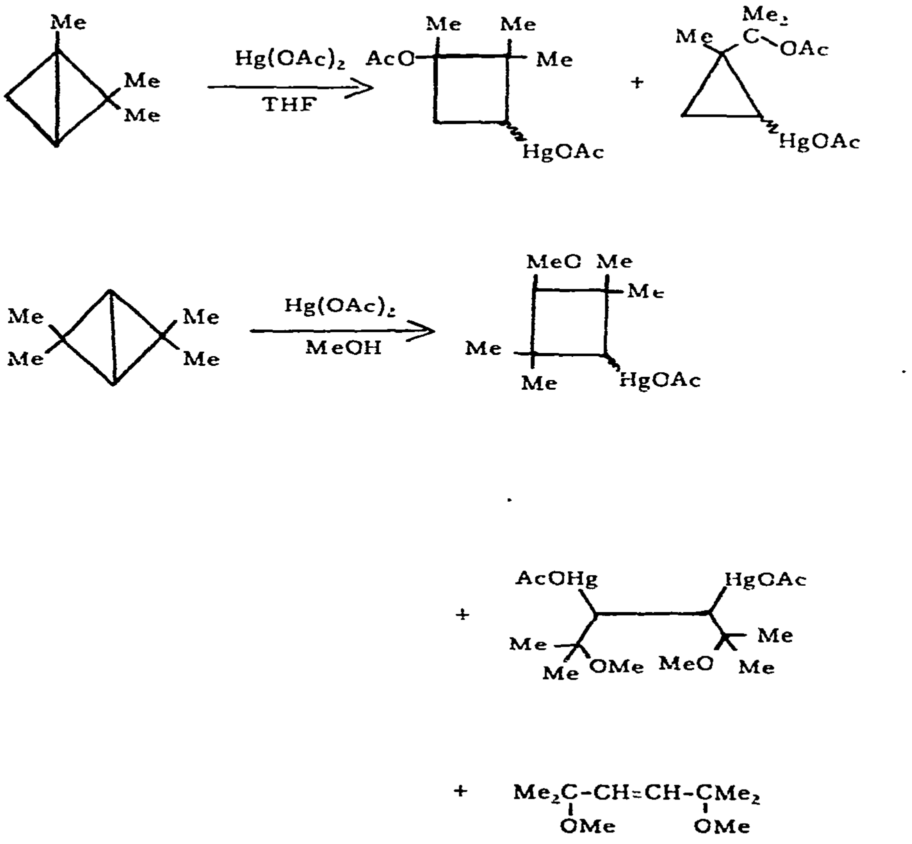
18

cis- and trans-Carane have been oxymercurated-demercurated (116). Stereospecific ring opening was observed:



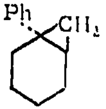


The stereochemistry of the ring opening of 1-phenylnorcarane was found to depend on the Hg(II) reagent used and on the solvent (Table 10) (117). These results were rationalized in terms of transition states or intermediates with a high degree of development of positive charge on the benzylic carbon atom. Also investigated has been the ring-opening oxymercuration of various bicyclo(1.1.0)butane derivatives (118, 119):



19

(Continued on p. 237)

Table 10. Stereochemistry of the Nucleophilic Step of the Mercuration of 

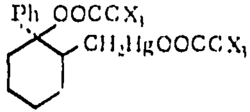
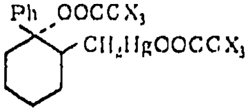
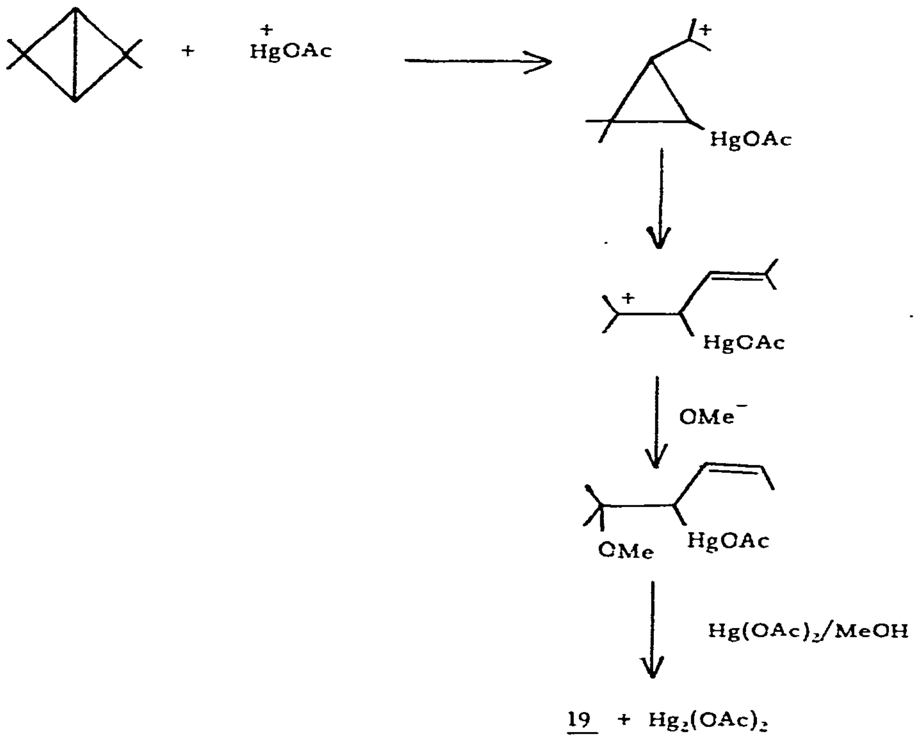
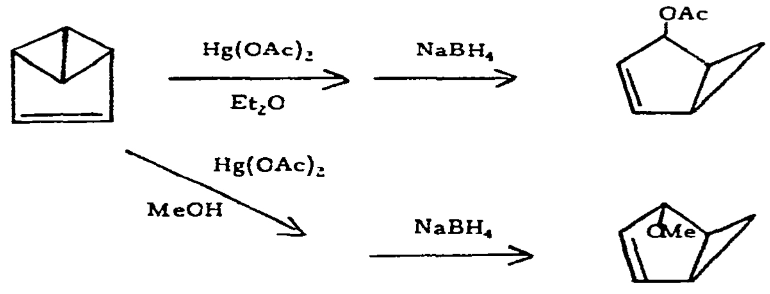
Hg(II) Salt	Added Nucleophile	Solvent	% 	% 
$Hg(OOCCH_3)_2$		H_2O	13.5	86.5
$Hg(OOCCF_3)_2$		H_2O	19.5	80.5
$HgSO_4$		H_2O	22.5	77.5
$Hg(NO_3)_2$		H_2O	22.5	77.5
$Hg(ClO_4)_2$		H_2O	23.0	77.0
$Hg(OOCCH_3)_2$		THF-H_2O (1:1)	25.5	74.5
$Hg(OOCCF_3)_2$		THF-H_2O (1:1)	28.5	71.5
$Hg(OOCCH_3)_2$		CH_3COOH	45.0	55.0
$Hg(OOCCH_3)_2$		CH_2Cl_2	58.0	42.0
$Hg(OOCCH_3)_2$	1 M CH_3COOH	CH_2Cl_2	54.5	45.5
$Hg(OOCCF_3)_2$		Cyclohexane	69.5	30.5
$Hg(OOCCF_3)_2$	H_2O (satd)	Cyclohexane	69.0	31.0
$Hg(OOCCF_3)_2$		CCl_4	62.0	38.0

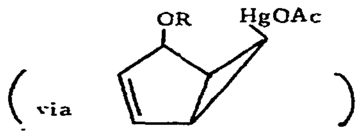
Table 10, continued

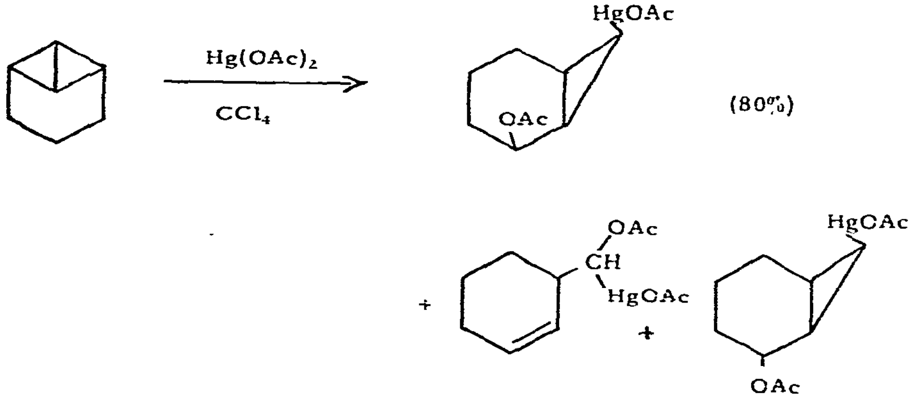
$Hg(OOCCF_3)_2$		$CHCl_3$	82.5	17.5
$Hg(OOCCF_3)_2$		CH_2Cl_2	75.0	25.0
$Hg(OOCCF_3)_2$	H_2O (satd)	CH_2Cl_2	73.0	27.0
$Hg(OOCCF_3)_2$		Benzene	71.0	29.0
$Hg(OOCCF_3)_2$	H_2O (satd)	Benzene	68.5	31.5
$Hg(OOCCF_3)_2$		CH_3NO_2	72.0	28.0

The formation of 19, the major product of the last reaction, was suggested to have occurred by the following route:

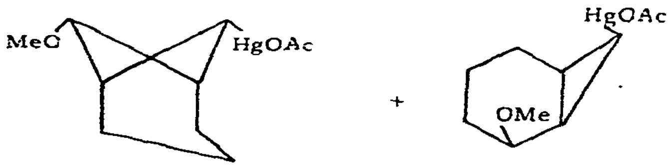


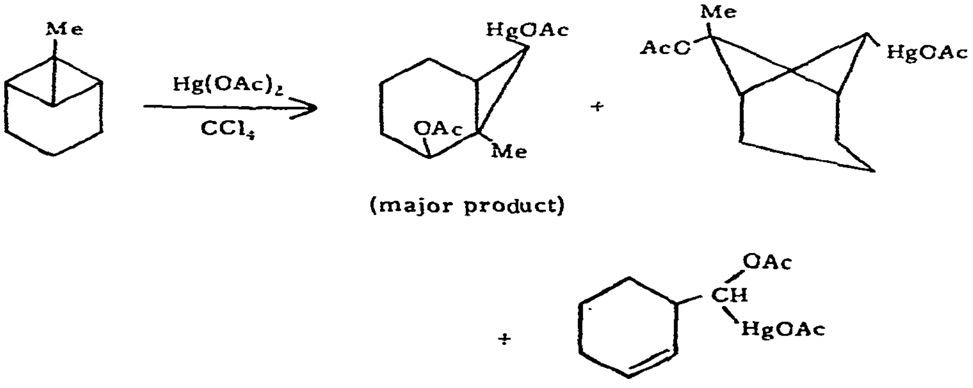


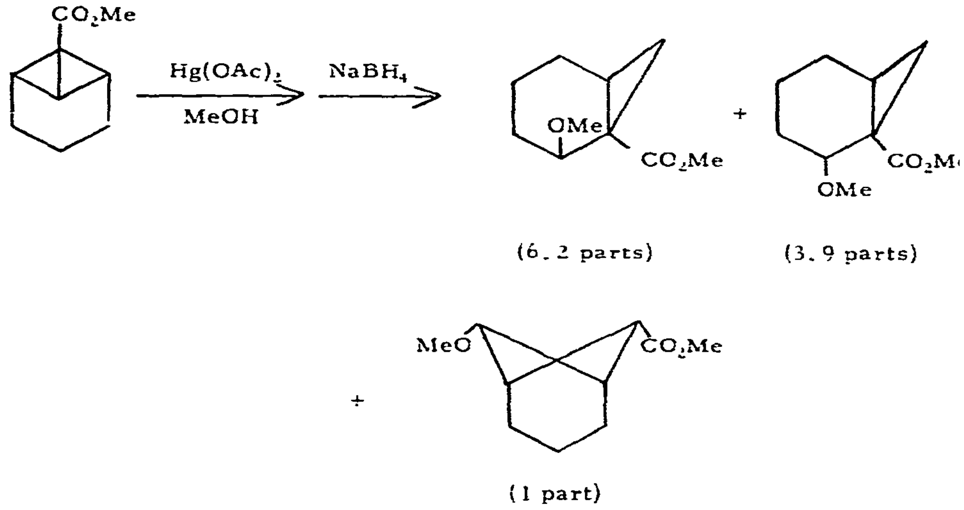




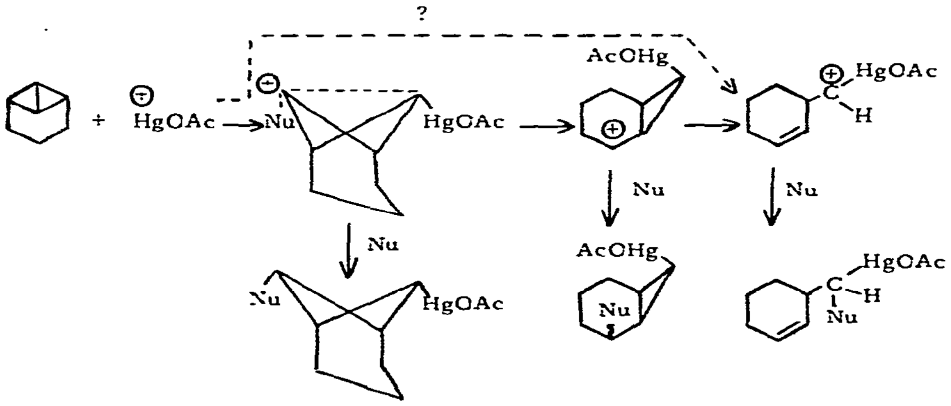
In methanol the same three products, as well as those shown below, were obtained:



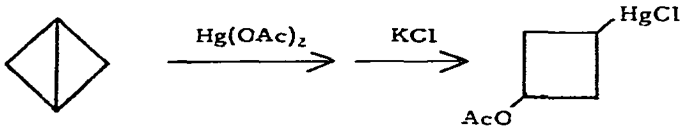




The mechanism of these reactions was discussed. The following pathway was suggested (Nu = nucleophile).

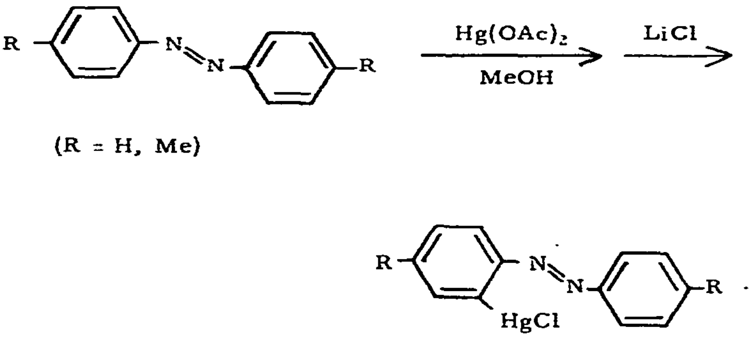


Russian workers (119a) have found that bicyclo(1.1.0) butane itself reacts with mercuric acetate in dichloromethane or carbon tetrachloride at 20° with cleavage of the central bond:

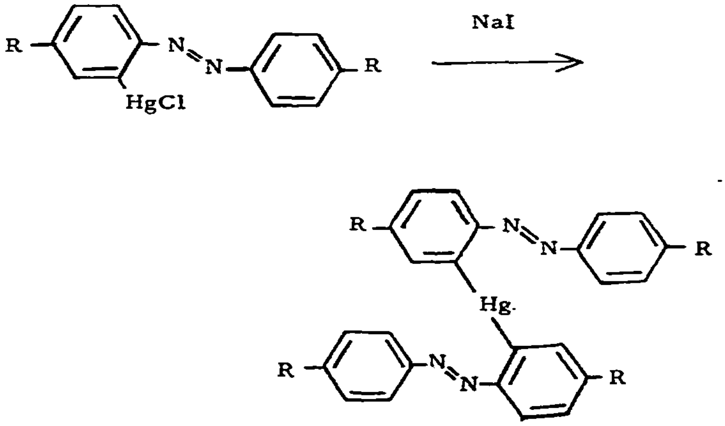


D. <u>Aromatic Compounds</u>

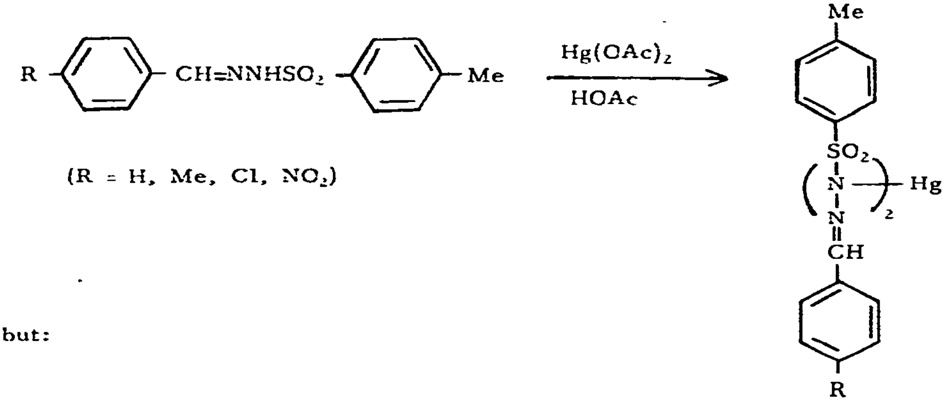
The mercuration of azobenzenes was reported in last year's survey (J. Organometal. Chem., 98 (1975) 222). Another group has used this reaction and has prepared the corresponding symmetrical mercurials (52):



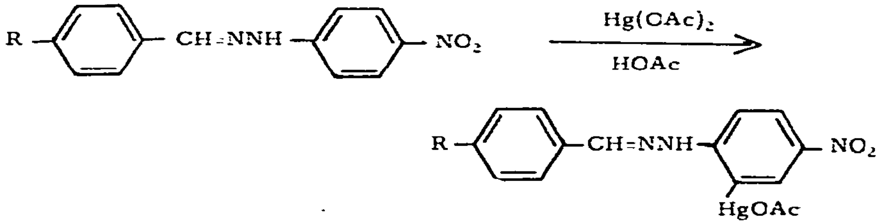
(R = H, Me)



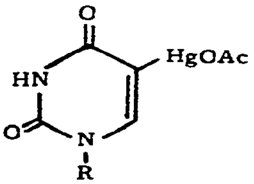
The reactions of mercuric acetate with aromatic hydrazones gave Hg-N derivatives or aromatic mercuration products, depending on the nature of the hydrazone (120):



but:



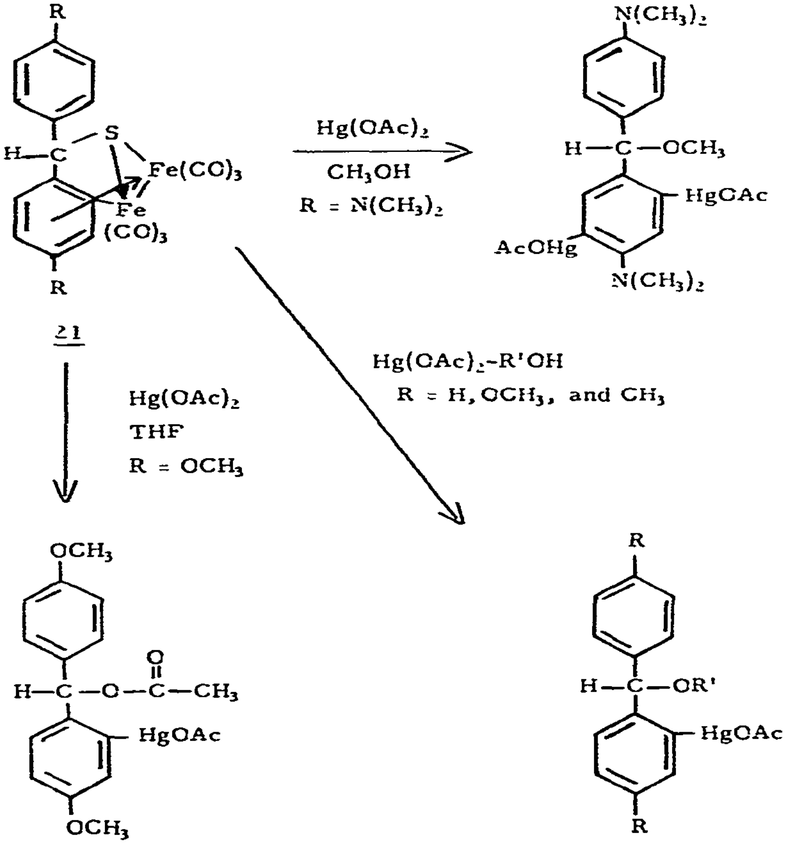
Mercury(II) compounds react with nucleotides such as uracil, uridine or thymidine in three different ways. One of these, observed on reaction of uridine-5'-triphosphate with aqueous mercuric acetate at 50° and pH 5, involves ring substitution to give a product of type 20 (121). The two other modes of reaction, observed with mercuric chloride and CH_3Hg^+ and such nucleotides, involved mercury coordination at nitrogen or oxygen.



20

Full details of the mercuration of 21 have been published (122) (cf. last year's survey, J. Organometal. Chem., 98 (1975) 225). The results are summarized in Scheme 3.

Scheme 3

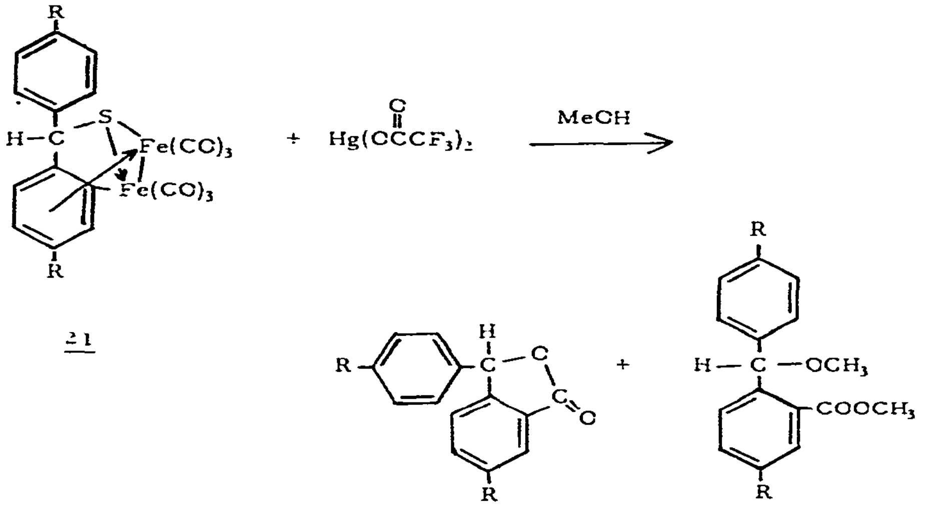


R = H; R' = CH$_3$

R = OCH$_3$; R' = CH$_3$

R = CH$_3$; R' = CH$_3$

R = OCH$_3$; R' = C$_2$H$_5$



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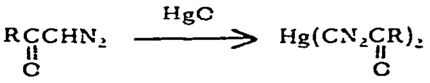
5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS

A. Mercurated Diazoalkanes

Treatment of α-diazoketones with mercuric oxide gave mercuribis(α-diazoketones) (123):



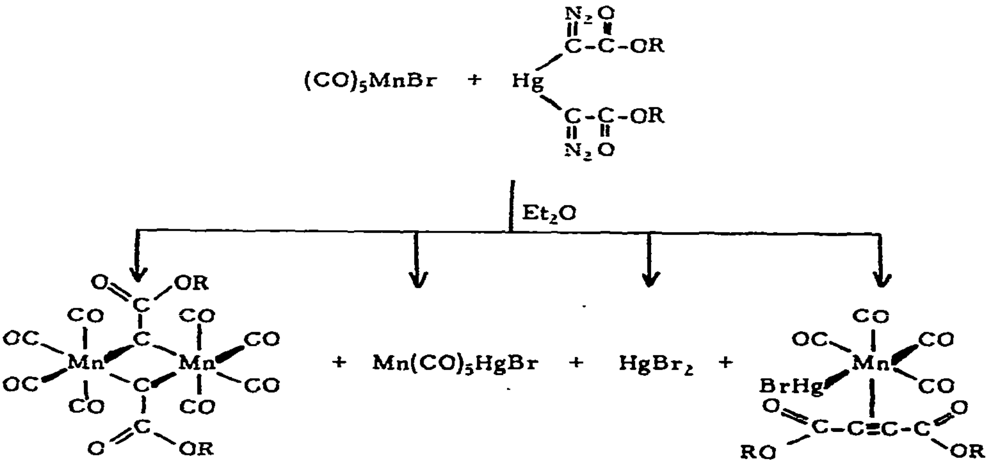
$$R\underset{\overset{\|}{O}}{C}CHN_2 \xrightarrow{HgO} Hg(CN_2\underset{\overset{\|}{O}}{C}R)_2$$

(R = Ph, mesityl, Me_3C, $PhCH_2$, Me, Et, i-Pr)

The IR, UV and ^1H and ^{13}C NMR spectra of these mercurials were investigated. The ^{13}C NMR signals for the diazo carbon atoms were found at remarkably high field (δ 52-93 ppm). The photolysis of $Hg(CN_2CO_2Et)_2$ in various chloroalkanes gave mercuric chloride and products derivable from insertion of CCO_2Et into C-Cl bonds (124):

Chloroalkane	Products	% Yield
CCl_4	$Cl_2C{=}(Cl)CO_2C_2H_5$	41
	$Cl_3CC(Cl)_2CO_2C_2H_5$	12
	Cl_3CCCl_3	52
CH_3CCl_3	$CH_3C(Cl){=}C(Cl)CO_2C_2H_5$	35
	$CH_3C(Cl)_2CH(Cl)CO_2C_2H_5$	37
	$CH_2{=}CCl_2$	18
$(CH_3)_2CCl_2$	$(CH_3)_2C{=}C(Cl)CO_2C_2H_5$	18
	$(CH_3)_2C(Cl)CH(Cl)CO_2C_2H_5$	7
	$ClCH_2CO_2C_2H_5$	35
	$CH_3C(Cl){=}CH_2$	24
$(CH_3)_3CCl$	$ClCH_2CO_2C_2H_5$	83
	$CH_2{=}C(CH_3)_2$	22

Mercurated diazoacetic esters, $Hg(CN_2CO_2R)_2$ (R = Et, Me_3C), were found to react with manganese pentacarbonyl bromide to give carbyne (CCO_2R)-derived organomanganese products (125):



B. Mercurated Carbonyl Compounds

Interest and activity in the chemistry and structures of mercurated β-diketones continues (cf. last year's survey, J. Organometal. Chem., 98 (1975) 230). Bonati and Minghetti have confirmed their synthesis of $(ClHg)_2C(COCH_3)_2$ (126). Its successful isolation is remarkably dependent on reaction conditions. In any case, there can be no doubt about the existence of this compound since its X-ray crystal structure has been determined (Fig. 3) (127).

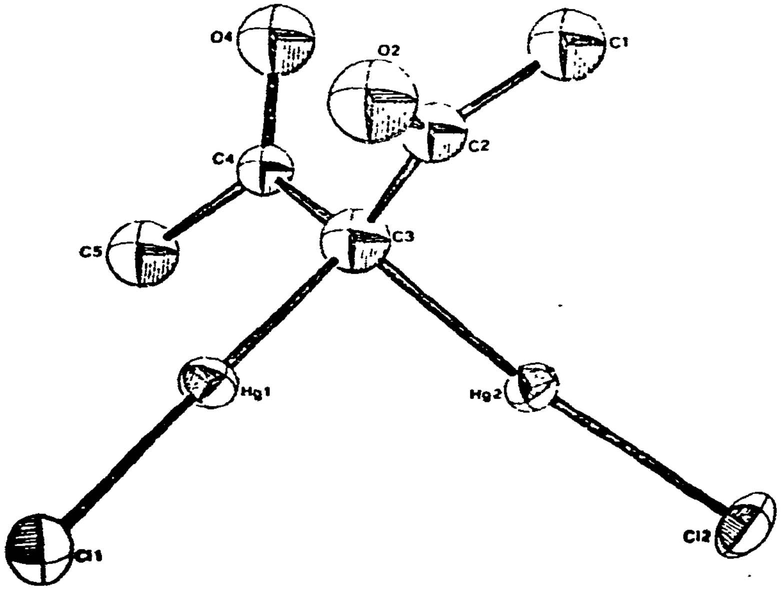
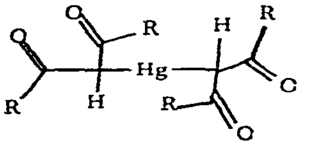


Figure 3. Molecular structure of 3,3-bis(chloromercuri)-2,4-pentanedione (ORTEP drawing). From L. E. McCandlish and J. W. Macklin, J. Organometal. Chem., 99 (1975) 31.

A study of bis(dipivaloylmethyl)mercury showed it to exist in solution principally as the monomer, 22 (128). In the solid state,



(R = Me_3C)

22

weakly bound dimers are present (Fig. 4). The chemistry of bis(di-

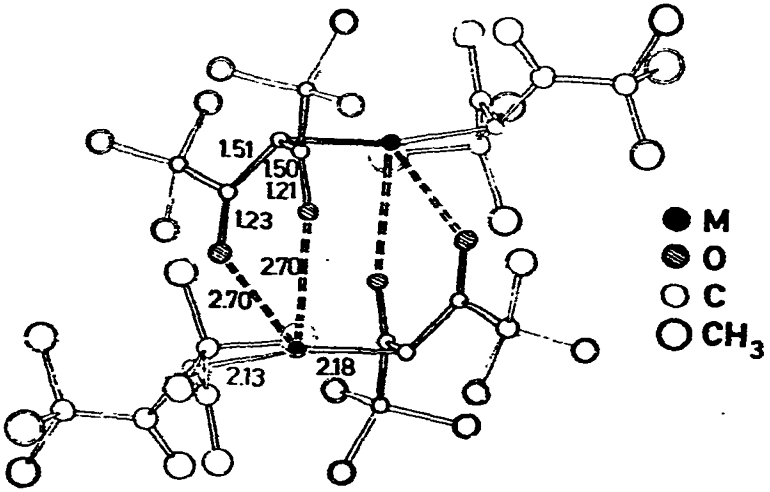
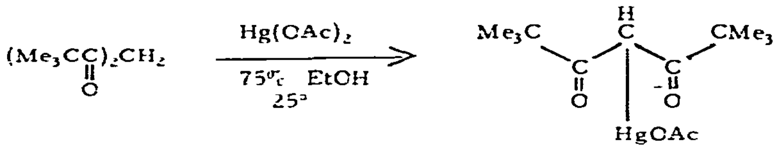


Figure 4. Structure of bis(dipivaloylmethyl)mercury. From K. Dietrich, H. Musso and R. Allmann, J. Organometal. Chem., 93 (1975) 15.

pivaloylmethyl)mercury and dipivaloylmethylmercuric acetate has received intensive study by Fish et al. (129). The chemistry which they developed is summarized in the equations below.

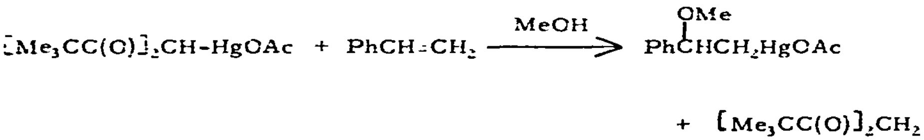


23

(Formation of 23 via addition of $AcOHg^+$ to the enol form of dipivaloylmethane was discussed).

$$2[Me_3CC(O)]_2CH\text{-}HgOAc \xrightarrow{H_2O} \{[Me_3CC(O)]_2CH\}_2Hg + Hg(OAc)_2$$

This equilibrium is driven to the right in water as a result of the insolubility of the bis(dipivaloylmethyl)mercury.



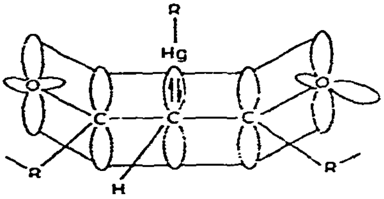
$$[Me_3CC(O)]_2CH\text{-}HgOAc + PhCH{=}CH_2 \xrightarrow{MeOH} Ph\overset{OMe}{C}HCH_2HgOAc + [Me_3CC(O)]_2CH_2$$

$$\{[Me_3CC(O)]_2CH\}_2Hg \xrightarrow{\text{UV in } CHCl_3} Hg_2(OAc)_2 + [Me_3CC(O)]_2CH_2$$

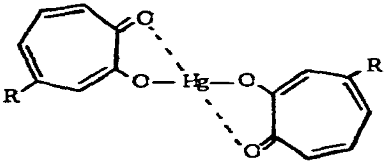
$$\{[Me_3CC(O)]_2CH\}_2Hg \underset{(X\,=\,Cl,\ OAc)}{\overset{HgX_2}{\rightleftharpoons}} 2[Me_3CC(O)]_2CHHgX$$

(K_{eq} = 620 for X = Cl; 1.3×10^5 for X = OAc)

An NMR study (129) suggested that the carbon-bonded mercury β - diketone derivatives of dipivaloylmethane are stabilized by σ-π-conjugation:

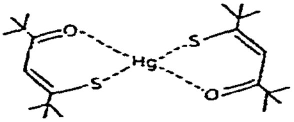


Mercury (II) tert-butyltropolonate was shown by means of IR and proton NMR spectroscopy to be Hg-C bonded (129):



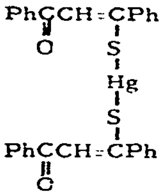
(R = Me_3C)

Two groups have investigated thio-β-diketone derivatives of Hg(II). These do not contain Hg-C bonds. On the basis of proton NMR and IR data, bis(thio-dipivaloylmethyl)mercury was formulated as 24, with much stronger Hg-S than Hg-O binding (128). ^{13}C and ^1H and IR



24

data obtained for bis(thio-dibenzoylmethyl)mercury were rationalized in terms of structure 25, with Hg-O interactions weak to nonexistent (130).



25

The very reactive mercuribisacetaldehyde serves well as starting material for the preparation of $Hg(CH_2COR)_2$ derivatives (131):

$$CH_2{=}C(R)OR' + Hg(CH_2CHO)_2 + 2\,H_2O \longrightarrow Hg(CH_2COR)_2$$

$$+ 2\,R'OH + CH_3CHO$$

(R = Me, Ph, p-MePh; R' = Et, $SiMe_3$)

Such mercuri-bisketones find use in the synthesis of enolic P(III) esters (132):

$$Hg(CH_2COR)_2 + (BuO)_2PH \xrightarrow{\text{py, }60\text{-}70^\circ} (BuO)_2POC(R){=}CH_2$$

(R = H, Me)

C. Organonitrogen Derivatives

Reaction of $(MeHg)_2O$ with acetonitrile or acetonitrile-d_3 was used in the preparation of $MeHgCH_2CN$ and $MeHgCD_2CN$ (133). The trismercurated product, $(MeHg)_3CCN$, was obtained by treatment of $MeHgCH_2CN$ with $(MeHg)_2O$ at 60° in vacuum.

Mercury derivatives of an imine have been prepared (134):

$$(\mathrm{AgC(OEt){=}NC_6H_4Me\text{-}p})_3 + (\mathrm{Ph_3P})_2\mathrm{HgCl_2} \xrightarrow{\mathrm{CHCl_3}}$$

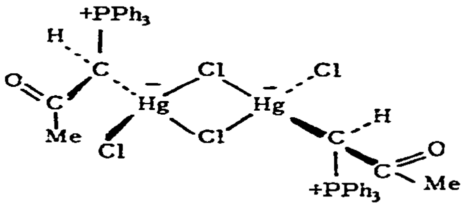
$$\mathrm{Hg(C(OEt){=}NC_6H_4Me\text{-}p)_2}$$

$$\Big\downarrow \mathrm{HgCl_2}$$

$$\mathrm{ClHgC(OEt){=}NC_6H_4Me\text{-}p}$$

D. Mercury-Substituted Ylides

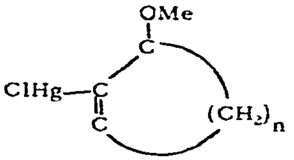
The formulation of mercury(II)-ylide complexes as ionic species, e.g., $[Ph_3\overset{+}{P}CH(HgCl)C(O)\dot{P}h]\ Cl^-$ (N. A. Nesmeyanov et al., 1965-1966) has been shown to be incorrect. In solution conductivity and solution molecular weight measurements provided evidence that such complexes are neutral, dimeric species (134a):



Similar complexes of mercuric chloride with $Ph_3P{=}CHCOPh$, $Ph_3P{=}CHCO_2Me$, $Ph_3P{=}CHCO_2Et$, $Ph_3P{=}C(COPh)_2$, $Ph_3P{=}C(Me)COPh$, $Ph_3P{=}C(Me)CO_2Et$, $Ph_3P{=}CHCN$, $Bu_3P{=}CHCOPh$, $Ph_3As{=}CHCOPh$, $Me_2S{=}CHCOPh$ and $C_5H_5N\text{-}CHCOPh$ were prepared and studied.

6. C-Hg BOND REACTIONS

The reduction of organomercurials to the hydrocarbon ($RHgX \longrightarrow RH + Hg + X^-$) has received continued study (cf. last year's survey, J. Organometal. Chem., 98 (1975) 232). Russian workers have investigated the reaction of organomercuric halides with sodium borohydride in various donor and nondonor solvents (135). The formation of an initial "coordination complex" was suggested, with subsequent further reaction by an electron-transfer pathway (to give RH, Hg and R_2Hg) and a competitive heterolytic pathway (to give RX). An electron-transfer process also was favored in the case of the reduction of RHgCl (R = Me_2CH, $PhCH_2$, Ph) with lithium deuteride (136). The Birch reduction (Na/liq. NH_3) of methoxymercuration products of allenes, 26, proceeded with retention of configuration (Table 11). An electron transfer mechanism was suggested (137).



26

(n = 6, 7, 8, 10)

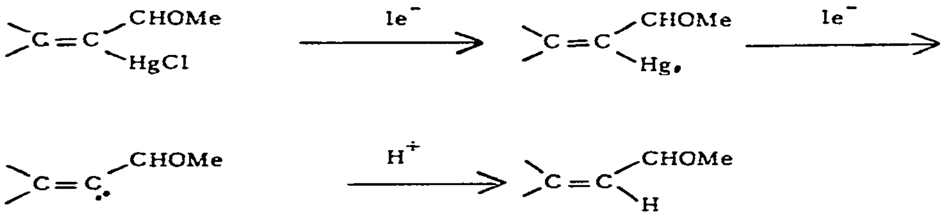
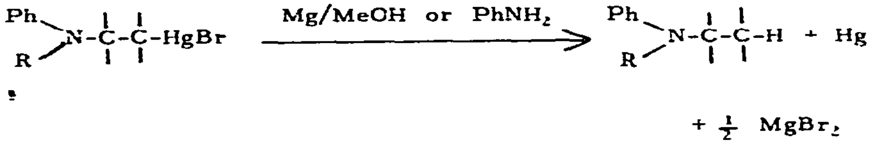


Table 11. Sodium-Ammonia Reduction of Cyclic Vinylic Organomercurials (ref. 137)

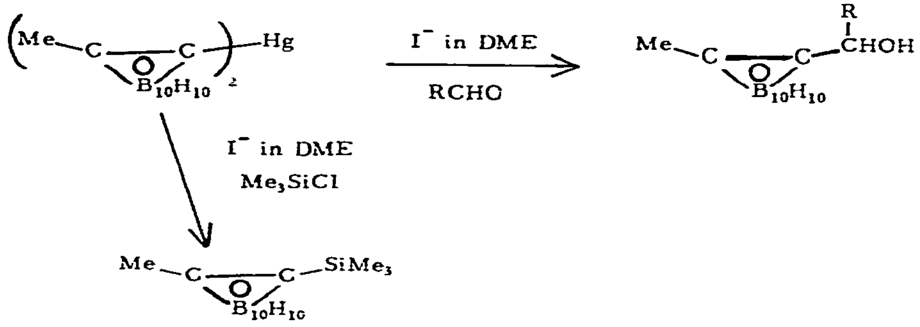
Compound	Products
cis-$C_{10}H_{17}OHgCl$ (C-9)	cis-3-Methoxycyclononene (86%)
	cis-Cyclononene (14%)
cis-$C_{11}H_{19}OHgCl$ (C-10)	cis-3-Methoxycyclodecene (85%)
	cis-Cyclodecene (15%)
trans-$C_{12}H_{21}OHgCl$ (C-11)	trans-3-Methoxycycloundecene (74%)
	cis-Cycloundecene (5%)
	trans-Cycloundecene (21%)
trans-$C_{14}H_{25}OHgCl$ (C-13)	trans-3-Methoxycyclotridecene (40%)
	cis-Cyclotridecene (16%)
	trans-Cyclotridecene (44%)

Organomercurial reduction also can be effected with magnesium in a protic solvent (138):



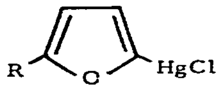
$$\mathrm{\overset{Ph}{\underset{R}{>}}N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}HgBr} \xrightarrow{\mathrm{Mg/MeOH\ or\ PhNH_2}} \mathrm{\overset{Ph}{\underset{R}{>}}N{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H} + \mathrm{Hg} + \frac{1}{2}\,\mathrm{MgBr_2}$$

Displacement of carbanions from organomercurials, R_2Hg, by iodide ion has been interpreted in terms of an electron transfer mechanism in which the radical anion, $R_2Hg^{\cdot -}$, is formed initially (139). It is of interest that iodide ion induces carboranyl anion addition at C=O and substitution at Si-Cl:



Hydrolysis of the C-Hg bond in certain organomercurials also is induced by iodide ion, as well as by N,N,N,N-tetramethyl-p-phenylenediamine. In the case of the latter, the amine radical cation is formed.

The rates of cleavage of furanylmercurials, 27, by iodine in



(R = Me, H, I,
Br, NO_2)

27

DMF/benzene have been studied; the rate constants correlated with σ_p^+ (140).

Further details have been published by Reutov and his coworkers on the oxidation of organomercurials with Cu(II) salts, in particular, $CuBr_2$, in DMF solution (cf. last year's survey, J. Organometal. Chem., 98 (1975) 240) (141).

$$R_2Hg \quad (\text{or } RHgBr) \xrightarrow[\text{no air}]{CuBr_2/DMF} RBr + HgBr_2 + CuBr$$

(R = Ph, C_6F_5, $C_6F_5CH_2$, $C_6H_5CH_2$, p-$MeOC_6H_4CH_2$, n-Bu, CCl_3, $(CF_3)_2CH$, $PhCOCH_2$, $PhCHCO_2Et$, $PhC{\equiv}C$)

Extensive discussion of possible mechanisms was given, with a process involving initial transmetalation followed by homolytic decomposition of the organocopper intermediate being favored.

The oxidation of $RHgCCl_3$ compounds (R = cyclohexyl, Ph, n-Pr, i-Pr) in various solvents (benzene, cyclohexane, heptane, chloroform) and at different temperatures was investigated by Russian workers (142). The corresponding RHgCl was the usually formed product, but in the case of n- and i-$PrHgCCl_3$, the decomposition was more complex, giving ROHgCl, Hg, $CHCl_3$ and CO as well.

Abstraction of a β hydride from alkylmercury compounds by triaryl carbonium ions has received considerable attention in the past few years, particularly from Reutov and his coworkers. This group now has studied the kinetics of such reactions (143):

$$(p\text{-}MeC_6H_4)_3C^+\ ClO_4^- + (C_2H_5)_2Hg \longrightarrow (p\text{-}MeC_6H_4)_3CH + C_2H_4 + C_2H_5HgClO_4$$

$$Ph_2(p\text{-}MeOC_6H_4)C^+\ ClO_4^- + (CH_3CH_2CH_2)_2Hg \longrightarrow Ph_2(p\text{-}MeOC_6H_4)CH + C_3H_6 + n\text{-}C_3H_7HgClO_4$$

In both reactions the process is rapid at the start, but further consumption of triarylmethyl perchlorate stops after a few minutes, presumably due to a retardation effect by $RHgClO_4$.

The cleavage of dibenzylmercury by a benzylsulfenium cation has been reported (144):

$$(PhCH_2)_2Hg + PhCH_2S^+\ BF_4^- \xrightarrow[-40^\circ]{ClCH_2CH_2Cl} [(PhCH_2)_2\overset{+}{S}\text{-}HgCH_2Ph]\ BF_4^- \quad (56\%)$$

An authentic sample of the product was prepared by the reaction:

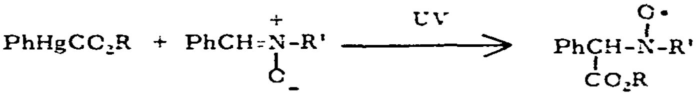
$$PhCH_2HgCl + (PhCH_2)_2S + AgBF_4 \longrightarrow [(PhCH_2)_2\overset{+}{S}-HgCH_2Ph]\ BF_4^-$$

Mercury-carbon bond cleavage was effected by the action of HCl on the charge transfer complex between benzylmercuric chloride and tetracyanoethylene, giving $PhCH_2C(CN)_2C(CN)_2H$ and $HgCl_2$ (145).

A germanium-thiol, $(C_6F_5)_3GeSH$, cleaved the Hg-C bond of diethylmercury (146):

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

The UV irradiation of methoxycarbonylmercury compounds results in homolytic fission of the Hg-C bond, as previous work has indicated. The $RC_2C\cdot$ radicals thus generated have been trapped using various nitrones (147):



$$PhHgCO_2R + PhCH{=}\underset{O^-}{\overset{+}{N}}{-}R' \xrightarrow{UV} Ph\underset{CO_2R}{C}H{-}\overset{O\cdot}{N}{-}R'$$

(R = Me, Et)
(R' = Me_3C, Ph)

Exchange reactions of organomercurials which involve redistribution of substituents on mercury have received much study in the past. Proton NMR and UV spectroscopy has been used to study such substituent exchange reactions of mixtures of symmetrical mercurials at room temperature in DMSO, pyridine and ethanol (149). The very reactive $Hg(CH_2CHO)_2$ undergoes facile exchange with diarylmercurials to give the respective unsymmetrical compound, $ArHgCH_2CHO$. Similar exchange was found to occur between pairs of diarylmercurials, but the unsymmetrical compounds were too labile to permit their isolation. No room temperature substituent exchange took place between Ph_2Hg and $(PhCH_2)_2Hg$ or $(PhCH_2CH_2)_2Hg$. A four-center transition state was assumed to be operative in these exchange reactions. The kinetics of similar redistribution systems were studied by Russian workers by a polarographic method (149):

$$Ar_2Hg \quad + \quad R_2Hg \rightleftharpoons 2\ ArHgR$$

$(Ar = Ph,\ p\text{-}MeOC_2H_4)$

The equilibria were displaced considerably to the right for mercurials where R = CN, CCl_3, C=CPh, $CClFCO_2Et$, CF_2CO_2Et, CH_2CO_2Me, CH_2Ph, and the reaction rate decreased in this order. Di-p-anisylmercury was considerably more reactive than diphenylmercury. In similar reactions of diarylmercurials with β-oxo mercurials, $Hg(CH_2COR)_2$ (R = H, Me, Ph, $p\text{-}MeC_6H_4$), equilibria were established:

$$Ar_2Hg \quad + \quad (RCOCH_2)_2Hg \rightleftharpoons 2\ ArHgCH_2COR$$

Ar = Ph	R = H	K_{eq} = 21
	Ph	15.5
	$p\text{-}MeC_6H_4$	9.5
	Me	5.4
Ar = $p\text{-}MeOC_6H_4$	R = H	K_{eq} = 32.5
	Ph	22
	$p\text{-}ClC_6H_4$	25.1
	$p\text{-}MeC_6H_4$	6.6
	Me	8.4

The position of such equilibria could be estimated using pK_a values of the RH compound corresponding to R_2Hg (150).

In another system:

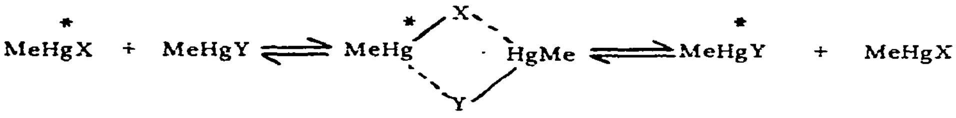
$$RHgX + Hg^{*}X_2 \longrightarrow RHg^{*}X + HgX_2 \qquad \text{(in EtOH)},$$

steric effects of the alkyl group R on relative rate constants have been calculated (151).

7. MERCURY-FUNCTIONAL MERCURIALS

Study of methylmercury species and equilibria using NMR and Raman spectroscopy showed $(MeHg)_3O^+$ to be only a minor component within a limited pH range in aqueous solution (152). This cation hydrolyzes to give MeHgOH and $(MeHg)_2OH^+$. The latter then reacts with hydroxide ion to product MeHgCH.

NMR studies of anion exchange between MeHgCN and MeHgX (X = Cl, OAc, Br, SCN, SMe, SPh, SC_6H_4Cl-p and $SCMe_3$) in DMF solution provided evidence against an ionic mechanism. A bridged intermediate or transition state, 28, was favored (153)

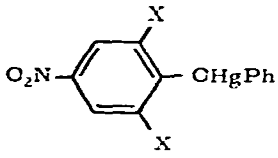


28

Ligand exchange between phenylmercuric acetate and various aryllead halides has been used as a preparative method for aryllead acetates (154):

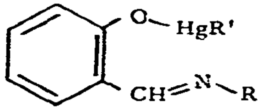
$$Ar_2PbBr_2 + 2\ PhHgOAc \xrightarrow{CHCl_3} Ar_2Pb(OAc)_2 + 2\ \underline{PhHgBr}$$

The degree of ionization of phenylmercuric p-nitrophenoxides, 29, has been measured spectrophotometrically (155). It decreased in the



29

order X = Cl > Br > I. The absorption and luminescence spectra (77°K to room temperature) of organomercury derivatives of hydroxy-araldimes, 30, 31, and of salicylaldehyde, 32, and p-hydroxybenzaldehyde, 33, have been investigated (156).



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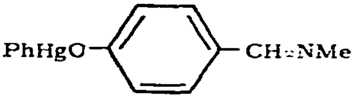
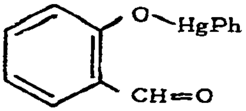


31

R	R'
Me	Me
Me	Ph
p-MeOC$_6$H$_4$	Ph



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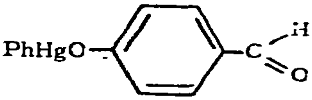
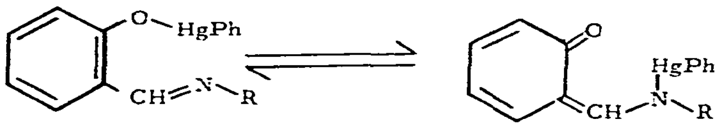
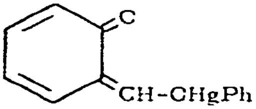


33

Compounds of type 30 were found to be present as an equilibrium mixture of tautomers:



Compounds 32 and 33 in DMSO are present in the quinoid form, 34 and 35, respectively.



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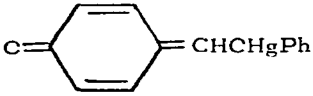


35

The thermal decomposition of a mercury peroxide, $EtHgOOCMe_2Ph$, has been examined in some detail. In hydrocarbon solution above 90° this compound appears to decompose by a homolytic pathway whose first step is O-O bond fission (157):

$$C_2H_5HgOOC(CH_3)_2C_6H_5 \longrightarrow C_2H_5HgO\cdot + C_6H_5(CH_3)_2CO\cdot$$

$$C_2H_5HgO\cdot \longrightarrow C_2H_5\cdot + HgO$$

$$C_6H_5(CH_3)_2CO\cdot \longrightarrow CH_3\cdot + C_6H_5COCH_3$$

$$C_2H_5HgO\cdot \xrightarrow{SH} C_2H_5HgOH + S\cdot$$

$$C_6H_5(CH_3)_2CO\cdot \xrightarrow{SH} C_6H_5(CH_3)_2COH + S\cdot$$

$$C_2H_5HgO\cdot + C_2H_5HgOOC(CH_3)_2C_6H_5 \longrightarrow C_2H_5HgOH + \cdot C_2H_4HgOOC(CH_3)_2C_6H_5$$

$$C_6H_5(CH_3)_2CO\cdot + C_2H_5HgOOC(CH_3)_2C_6H_5 \longrightarrow C_6H_5(CH_3)_2COH$$

$$+ \cdot C_2H_4HgOOC(CH_3)_2C_6H_5$$

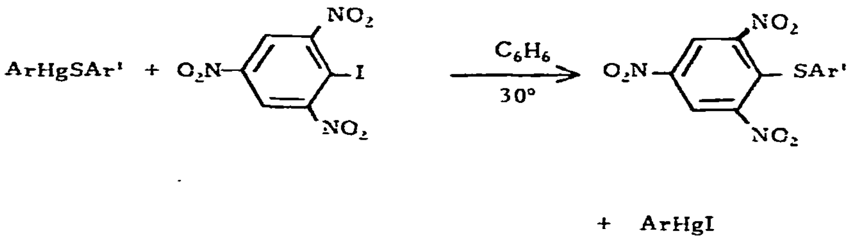
$$\cdot C_2H_4HgOOC(CH_3)_2C_6H_5 \longrightarrow C_2H_4 + HgO + C_6H_5(CH_3)_2CO\cdot$$

and

$$2C_2H_5HgOH \longrightarrow (C_2H_5)_2Hg + HOHgOH$$

In carbon tetrachloride at 110° this peroxide decomposed to give Hg_2Cl_2, EtHgCl, $PhMe_2COH$, $CH_2{=}CMePh$, MeCOPh, PhOH, Me_2CO, $CHCl_3$, CO_2, C_2H_4 and C_2H_6 (158). Its reaction with lauroyl peroxide at 20-50° resulted in formation of ethylmercuric lauroyl peroxide, α-cumyl peroxylaurate, $PhMe_2COH$, CO_2, O_2 and CH_4 (159). The intervention of both a radical and a molecular mechanism was suggested.

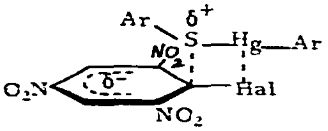
The reaction of aryl arylmercury sulfides with picryl iodide has received further study (160):



Ar	Ar'
p-MeC_6H_4	Ph
m-MeC_6H_4	Ph
Ph	Ph
p-ClC_6H_4	Ph
m-ClC_6H_4	Ph
o-MeC_6H_4	Ph

2,4,6-$Me_3C_6H_2$	Ph
Ph	p-MeC_6H_4
Ph	m-MeC_6H_4
Ph	p-ClC_6H_4
Ph	m-ClC_6H_4
Ph	o-MeC_6H_4
Ph	2,4,6-$Me_3C_6H_2$

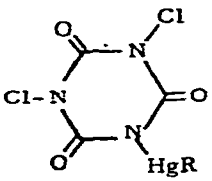
Electron-donating substituents in Ar and Ar' accelerate, electron-withdrawing substituents retard the rate of reaction. For substituents in Ar, log rate vs σ gave $\rho = -0.966$; for substituents in Ar', a similar correlation gave $\rho = -3.67$. Transition state 36 was suggested.

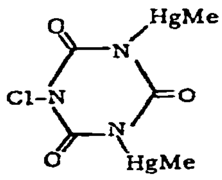


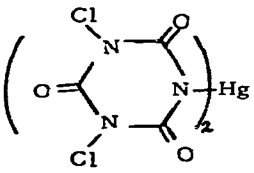
36

Hg-S bonding was shown to occur (by means of ^1H and ^{13}C NMR) in $CH_3Hg(I)$ derivatives of cysteine, penicillamine and the tripeptide glutathione (161).

The reaction of cyanuric chloride with mercuric chloride, methylmercuric chloride and dimethylmercury in acetonitrile at 80° gave Hg-N derivatives (162):

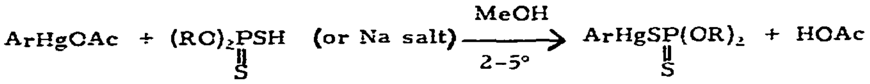






(R = Cl, Me)

Arylmercury dialkylphosphorodithioates have been prepared (163):



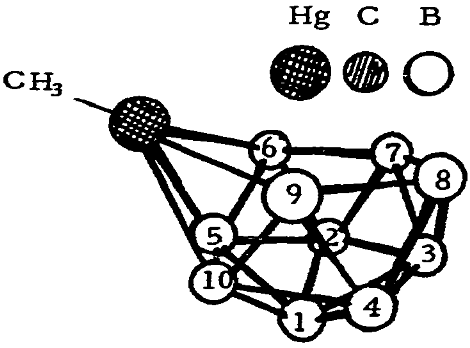
$$\mathrm{ArHgOAc} + (\mathrm{RO})_2\underset{\underset{\displaystyle S}{\|}}{P}\mathrm{SH}\ \text{(or Na salt)} \xrightarrow[2-5°]{\mathrm{MeOH}} \mathrm{ArHgS}\underset{\underset{\displaystyle S}{\|}}{P}(\mathrm{OR})_2 + \mathrm{HOAc}$$

(Ar = Ph, p-$H_2NC_6H_4$;
R = Me, Et, n-Pr, i-Pr, Ph)

A methylmercury derivative of the dodecahydro-nido-decaborate (2-) anion has been reported (164):

$$\mathrm{Me_2Tl}^+[\mathrm{B_{10}H_{12}TlMe_2}]^- + \mathrm{MeHgCl} \xrightarrow{\mathrm{THF}} \xrightarrow{\mathrm{Ph_3PMe^+Br^-}} [\mathrm{Ph_3PMe}]^+ [\mathrm{B_{10}H_{12}HgMe}]^-$$

The product is an air-stable, orange, crystalline solid. ^{11}B NMR spectroscopy suggested a structure with the CH_3HgB_{10} framework shown, 37.



37

Methylmercury derivatives of phthalocyanines and tetraphenylporphyrin have been reported (165).

Also worth noting are the use of $[(CF_3)_2NO]_2Hg$ in the preparation of $(CF_3)_2NO$-substituted silanes (166), of $Hg(SeCF_3)_2$ in the synthesis of $B(SeCF_3)_3$ (167) and of $Hg(SCN)_2$ in the synthesis of organic isothiocyanates in reactions with organic halides (168).

8. MERCURY-GROUP IV COMPOUNDS

The structure of octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane has been determined by X-ray diffraction (Fig. 5) (169).

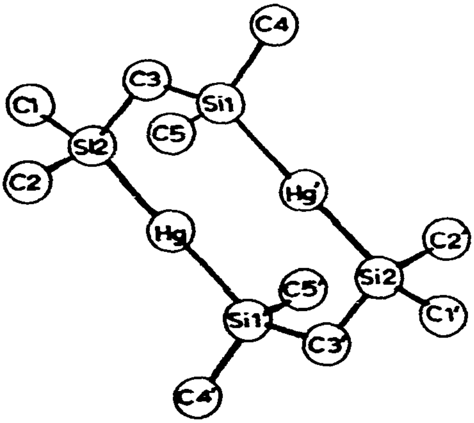


Figure 5. The skeletal structure of octamethyl-2,4,6,8-tetrasila-1,5-dimercuracyclooctane (from M. J. Albright, T. F. Schaaf, W. M. Butler, A. K. Hovland, M. D. Glick and J. P. Oliver, J. Amer. Chem. Soc., 97 (1975) 6261)

The Si-Hg-Si bond angle is 178.7°. Lithium tetrakis(dimethylphenylsilyl)mercurate, $Li_2[Hg(SiMe_2Ph)_4]$, was shown (X-ray diffraction) to contain isolated contact ion pairs (169). The mercury atom in the anion is tetrahedrally coordinated by four silyl groups. Figure 6 shows the essential features of the contact ion pair.

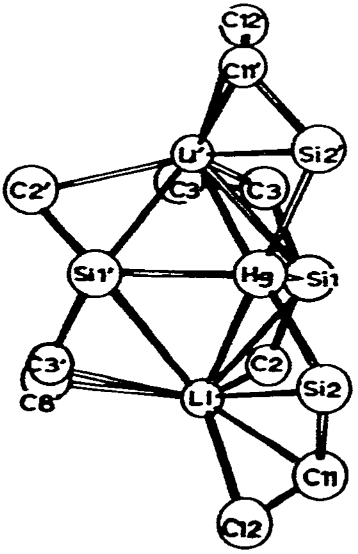


Figure 6. A partial structural representation of lithium tetrakis-(dimethylphenylsilyl)mercurate showing the coordination of the lithium ions. C2 and C2' are methyl carbon atoms; the other carbons belong to phenyl substituents (from M.J. Albright, T. F. Schaaf, W. M. Butler, A. K. Hovland, M. D. Glick and J. P. Oliver, J. Amer. Chem. Soc., 97 (1975) 6261)

Some new silyl- and germyl-mercurials have been prepared. English workers have reported the synthesis of $Me_3SiHgSiH_3$, $(H_3Si)_2Hg$, $Me_3SiHgGeH_3$ and $(H_3Ge)_2Hg$ (170):

$$(Me_3Si)_2Hg\ \ (solid) + H_3SiBr \longrightarrow Me_3SiBr + Me_3SiHgSiH_3$$

$$(Me_3Si)_2Hg + 2\ H_3SiBr \xrightarrow{\text{in solution}} (H_3Si)_2Hg + 2\ Me_3SiBr$$

Similar reactions served in the preparation of the germanium-containing compounds.

The rather light-sensitive $(Me_2ClSi)_2Hg$ has been isolated from the reaction of Me_2HSiCl with di-tert-butylmercury at 85° (171). This compound is thermally stable enough to sublime at 80° and was found to exchange Me_2ClSi groups in solution in a second order rate process. Another new silyl-mercurial is $[(PhCH_2)_3Si]_2Hg$ (172):

$$2\ (PhCH_2)_3SiH + Et_2Hg \xrightarrow{190^\circ} 2\ C_2H_6 + [(PhCH_2)_3Si]_2Hg$$

Its chemical reactions were studied:

$$\begin{aligned}
[(PhCH_2)_3Si]_2Hg &\xrightarrow{\Delta} (PhCH_2)_6Si_2 + Hg \\
&\xrightarrow[\text{heat}]{O_2,\ \text{xylene}} (PhCH_2)_3SiOSi(CH_2Ph)_3 + Hg \\
&\xrightarrow{BrCH_2CH_2Br} 2\ (PhCH_2)_3SiBr + Hg + C_2H_4 \\
&\xrightarrow{HgBr_2} 2\ (PhCH_2)_3SiBr + 2\ Hg \\
&\xrightarrow[(X\ =\ Cl,\ OEt)]{Et_3SnX} 2\ (PhCH_2)_3SiX + Hg + Et_6Sn_2
\end{aligned}$$

The reaction of EtHgCl with $(C_6F_5)_6Ge_2$ in THF at 70° gave the unsymmetrical mercurial $(C_6F_5)_3GeHgEt$ (173).

The mechanism of the photolysis of bis(trialkylsilyl)- and bis-(trialkylgermyl)mercurials has been the subject of a thorough investigation by Neumann and his coworkers (174). Initial photochemical generation of free radicals, $R_3M\cdot$, and mercury is followed by a chain reaction involving an S_H2 reaction at the silicon:

initiation:

$$(Me_3Si)_2Hg \longrightarrow Me_3Si\cdot \;+\; \cdot Hg\text{-}SiMe_3 \longrightarrow Hg \;+\; 2\,Me_3Si\cdot$$

chain propagation:

$$Me_3Si\cdot \;+\; (Me_3Si)_2Hg \longrightarrow \left[\begin{array}{l} Me_3Si\text{----}Hg\text{-}SiMe_3 \\ \quad\vdots \\ Me_3Si \end{array}\right]^{\pm\,\cdot}$$

$$\searrow$$

$$Me_3SiSiMe_3 \;+\; Hg \;+\; Me_3Si\cdot$$

The chain reactions are inhibited by $Me_3Si\cdot$ radical scavengers such as secondary and tertiary alkyl halides, but the disilane still is formed due to cage effects. The radical $Me_3SiHg\cdot$ has a very short lifetime at best and may not have a separate existence at all. S_H2 reactions at mercury also occur:

$$\overset{*}{Me_3Si}\cdot \;+\; (Me_3Si)_2Hg \longrightarrow \overset{*}{Me_3Si}\text{-}Hg\text{-}SiMe_3 \;+\; Me_3Si\cdot$$

A proven radical chain process (S_H2 at mercury) is the reaction of

$(Me_3M)_2Hg$ (M = Si, Ge) with primary alkyl chlorides and bromides upon daylight irradiation (175):

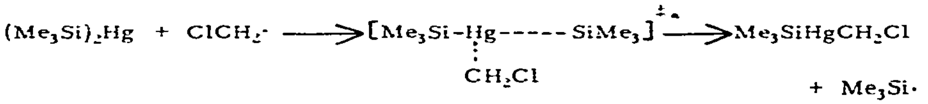
$$(Me_3M)_2Hg + RX \xrightarrow{h\nu} Me_3MHgR + Me_3MX$$

(R = $CHCl_2$, CH_2Cl, Me, Et,
n-Pr, n-Bu)

Using the reaction with dichloromethane as an example, the reaction course is as follows:

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

$$Me_3Si\cdot + CH_2Cl_2 \longrightarrow ClCH_2\cdot + Me_3SiCl$$



$$(Me_3Si)_2Hg + ClCH_2\cdot \longrightarrow \left[Me_3Si\text{-}\underset{\underset{CH_2Cl}{\vdots}}{Hg}\text{-----}SiMe_3\right]^{\ddagger\bullet} \longrightarrow Me_3SiHgCH_2Cl + Me_3Si\cdot$$

Such S_H2 reactions were not observed with tert-butyl, isopropyl, cyclohexyl and benzyl halides. Carbon tetrachloride, chloroform, trityl chloride and vicinal dibromides react with $(Me_3M)_2Hg$ without irradiation, e.g.:

$$(Me_3Si)_2Hg + CCl_4 \xrightarrow{-20^\circ} [Me_3SiHgCCl_3] \longrightarrow Me_3SiCCl_3 + Hg$$

$$(Me_3Si)_2Hg + BrCH{=}CHBr \xrightarrow{20^\circ} Hg + HC{\equiv}CH + 2\ Me_3SiBr$$

$$(Me_3Si)_2Hg + Br(CH_2)_3Br \longrightarrow Hg + 2\ Me_3SiBr + cyclo\text{-}C_3H_6$$

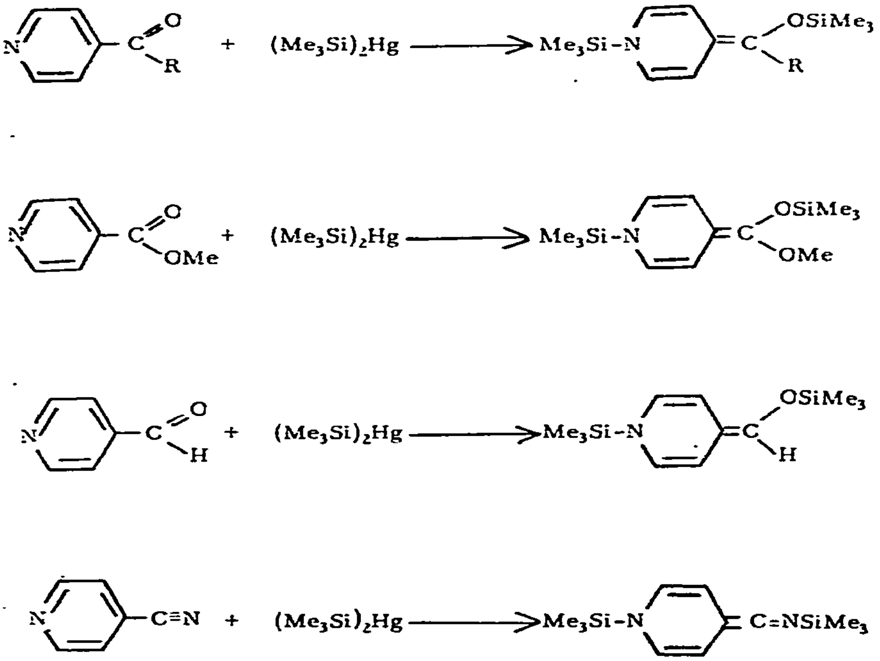
Photo-induced reactions of $(Me_3M)_2Hg$ (M = Si, Ge) with aryl bromides in excess give diarylmercurials:

$$(Me_3Si)_2Hg + 2\ ArBr \xrightarrow[h\nu]{\text{room temp.}} Ar_2Hg + 2\ Me_3SiBr + Hg$$

$(Ar = Ph,\ p\text{-}MeC_6H_4,\ 2,4,6\text{-}Me_3C_6H_2,\ 1\text{-}C_{10}H_7)$

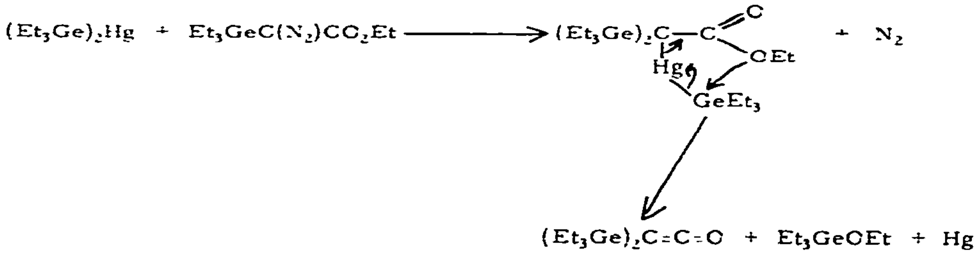
The available evidence speaks strongly for a radical chain process.

Bis(trimethylsilyl)mercury has been used to generate ketyl radicals of type $RR'\dot{C}\text{-}OSiMe_3$ by thermal or photo-induced reactions with ketones and aldehydes (176). Reactions of $(Me_3Si)_2Hg$ with pyridines containing conjugative groups such as CO_2Me, COMe, COPh and CN in position 4 have been studied (177). Colored, ESR-detectable radical intermediates were involved in these reactions.



A molecular mechanism apparently is involved in the reactions of bis(triphenylsilyl)mercury with hydroxy compounds. These gave hydrogen, triphenylsilyl ethers and elemental mercury as the major products (178). Triphenylsilane was a minor product. The reaction with water proceeded rapidly at ambient temperature, but those with n-octyl alcohol, cyclohexanol and phenol required reaction temperatures of 120°, 140° and 220°, respectively.

The reaction of bis(triethylgermyl)mercury with the triethylgermyl derivative of ethyl diazoacetate provided a novel synthesis of bis(triethylgermyl)ketene (179). A reaction course proceeding via insertion of Et_3GeCCO_2Et into the Ge-Hg bond was written:



Further work has been devoted to the reactions of silylmercury compounds with alkali metals to give silyl-alkali compounds. In benzene the reaction of $(Et_3Si)_2Hg$ with sodium gave metallic mercury, Et_3SiPh, Et_3SiH, phenylsodium, sodium hydride and Et_3SiNa. With potassium, Et_3SiPh, metallic mercury and potassium hydride resulted. It is evident that the Et_3SiM reagents attack the benzene solvent (180). $Et_3SiHgSi_2Et_5$ reacted similarly. A reaction of $(Et_3Si)_2Hg$ with potassium carried out in toluene gave mercury, benzyltriethylsilane, triethylsilane and benzylpotassium. Triethylsilane was found to be a useful solvent for the $(Et_3Si)_2Hg/K$ reaction at room temperature since it reacts only slowly with such reagents under those conditions. When the $(Et_3Si)_2Hg/K$ reaction was carried out in the presence of vinyltrimethylsilane, a portion of the Et_3SiK formed was trapped by reaction with the vinylsilane (181).

More reactions of Group IV mercurials with transition metal derivatives have been reported. Such reactions are excellent routes to Group IV element-transition metal bonded compounds (182):

$$(R_3Sn)_2Hg + [\pi\text{-}C_5H_5Fe(CO)_2]_2 \longrightarrow 2\ \pi\text{-}C_5H_5Fe(CO)_2SnR_3 + Hg$$

$$+ [\pi\text{-}C_5H_5NiCO]_2 \longrightarrow 2\ \pi\text{-}C_5H_5Ni(CO)SnR_3 + Hg$$

$$+ [\pi\text{-}C_5H_5Mo(CO)_3]_2 \longrightarrow 2\ \pi\text{-}C_5H_5Mo(CO)_3SnR_3 + Hg$$

$$(R_3Ge)_2Hg + Hg[Co(CO)_4]_2 \longrightarrow 2\ R_3GeCo(CO)_4 + 2\ Hg$$

($R = Me_3SiCH_2$ in all reactions)

With $(\pi\text{-}C_5H_5)_2TiCl_2$ reduction occurred (183):

$$(Et_3Ge)_2Hg + (\pi\text{-}C_5H_5)_2TiCl_2 \longrightarrow (\pi\text{-}C_5H_5)_2TiCl + Hg + 2\ Et_3GeCl$$

Reactions of bis(trimethylsilyl)mercury with triorganotin derivatives proceed <u>via</u> $(R_3Sn)_2Hg$ intermediates, which, however, are unstable under the reaction conditions (184):

$$(Me_3Si)_2Hg + 2\ R_3SnX \longrightarrow R_3SnSnR_3 + 2\ Me_3SiX + Hg$$

($X = OMe, OEt, OAc, OSnEt_3, OSiMe_3, NEt_2, Cl, Br, H$;
$R = Me, Et, Bu, Ph$)

When X = OR, OAc, and $OSnEt_3$, the reactions were rapid and exothermic; when X = $OSiMe_3$, halogen, H, and NEt_2, longer reaction times at 80° were required. Similar reactions were carried out with R_2SnX_2 compounds. Oligomeric $(R_2Sn)_n$ products were obtained. Compounds of type R_2SnXY reacted with $(Me_3Si)_2Hg$ to give distannanes:

$$2\ R_2SnXY\ +\ (Me_3Si)_2Hg \longrightarrow 2\ Me_3SiX\ +\ Hg\ +\ YR_2SnSnR_2Y$$

(X OMe, OAc; Y Br, Cl)

Intermediates with Sn-Hg bonds are believed to be involved in reactions of hexamethylditin with alkylmercuric halides and mercuric halides (185):

$$Me_6Sn_2\ +\ RHgX \longrightarrow Me_3SnX\ +\ Me_3SnHgR$$

$$Me_3SnHgR \longrightarrow Me_3SnR\ +\ Hg$$

$$Me_3SnHgR\ +\ RHgX \longrightarrow Me_3SnX\ +\ R_2Hg\ +\ Hg$$

(R = Me, CD_3, $CH_2{=}CH$, trans-ClCH=CH, Me_3C)

Products of the type shown in the last two equations were isolated.

9. COMPLEXES OF ORGANOMERCURIALS

An X-ray crystal structure determination of $(MeHgbipy)^+NO_3^-$ showed the presence of an unsymmetrically chelated ligand; the $CHgN_2$ grouping is planar (Fig. 7) (186). Other similar complexes were

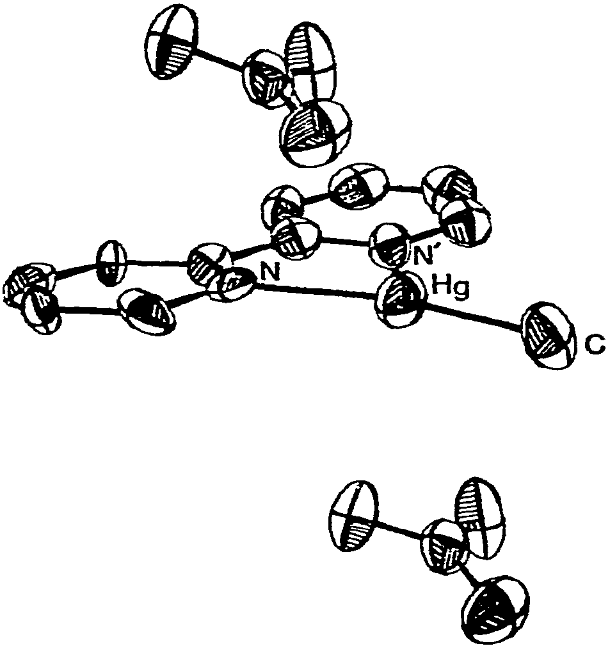


Figure 7. Structure of [MeHg(2,2'-bipyridyl)]$^{+}$NO$_3^{-}$ showing the positions of neighboring nitrate ions (from A. J. Canty, A. Marker and B. M. Gatehouse, J. Organometal. Chem., 88 (1975) C31)

prepared (Table 12). The magnitude of the ^{1}H-^{199}Hg coupling constants observed in the NMR spectra of these compounds is indicative of the coordination number of mercury: CN2, 227-230 Hz; CN3 235-240 Hz. Thus the sterically hindered 3,3'-dimethylbipyridine acts as a monodentate ligand.

^{19}F NMR studies of carbon tetrachloride solutions of polyfluoroalkylmercurials [$(CF_3)_2Hg$, $(C_2F_5)_2Hg$, $[(CF_3)_2CF]_2Hg$, $(CF_3CH_2)_2Hg$] containing Lewis bases (pyridine, butylamine, ethylenediamine, THF, DME, dioxane) demonstrated the presence of 1:2 R_2Hg/Lewis base solvates

Table 12. ^{1}H NMR Parameters for the Methylmercury Group in the Complexes^a

Complex	δ(MeHg)^b	J(^{1}H-^{199}Hg)
$MeHgNO_3$	2.597	251.8
[MeHg(py)]NO_3	2.564	229.6
[MeHg(2-mpy)]NO_3	2.533	227.9
[MeHg(3-mpy)]NO_3	2.589	228.2
[MeHg(4-mpy)]NO_3	2.585	227.5
[MeHg(bipy)]NO_3	2.499	238.8
[MeHg(6,6'-dmbipy)]$NO_3\cdot H_2O$	2.508	235.9
[MeHg(5,5'-dmbipy)]NO_3	2.518	237.1
[MeHg(4,4'-dmbipy)]NO_3	2.550	235.1
[MeHg(3,3'-dmbipy)]NO_3	2.893	230.4
[MeHg(phen)]NO_3	2.383	239.8
[MeHg(2,9-dmphen)]$NO_3\cdot H_2O$	2.384	236.0

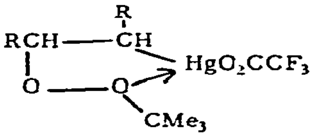
a. 0.1M solutions in CD_3OD at 100 MHz.

b. Chemical shift upfield from internal 1,4-dioxane, accuracy to ca. ± 0.005 ppm.

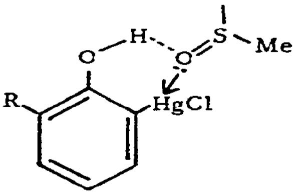
2-mpy = 2-methylpyridine. 6,6'-dmbipy = 6,6'-dimethyl-2,2'-bipyridyl. 2,9-dmphen= 2,9-dimethyl-1,10-phenanthroline. Other ligands similarly abbreviated.

(or 1:1 if the Lewis base was bidentate) (187). In similar fashion, ^{31}P NMR spectroscopy served to show that such polyfluoroalkylmercurials coordinate two tertiary phosphine molecules (or one bidentate diphosphine) in dichloromethane solution (188). Variable temperature NMR studies demonstrated that exchange occurs between coordinated and free phosphines

Proton NMR studies provided evidence for intramolecular O ⟶ Hg coordination in β-peroxymercurials:



The addition of pyridine to a solution of such a mercurial destroyed such intramolecular interactions in favor of intermolecular coordination at mercury by pyridine (97). An IR study of o- and p-chloromercuriphenols in donor solvents (DMSO, HMPT) provided an indication that complexes of type 38 occur (189).



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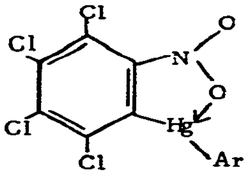
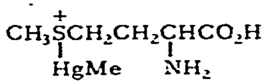
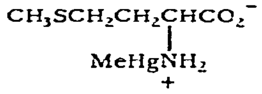
An IR spectroscopic study of bis(2,3,4,5-tetrachloro-6-nitrophenyl)-mercury suggested that intramolecular O⟶Hg coordination was a possibity (22):



According to proton NMR results, $CH_3Hg(I)$ binds to the thioether group of methionine in acidic solution and to the amino group in basic solution (190):

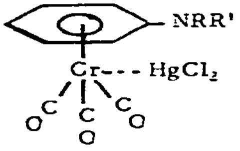

$CH_3\underset{\displaystyle |\atop HgMe}{\overset{+}{S}}CH_2CH_2\underset{\displaystyle |\atop NH_2}{C}HCO_2H$ in acidic solution;


$CH_3SCH_2CH_2\underset{\displaystyle |\atop MeHgNH_2^{+}}{C}HCO_2^-$ in basic solution

Complexes of mercuric cyanide with 2,2'-bipyridine, o-phenanthroline and 2,9-dimethyl-o-phenanthroline have been reported (191).

^{199}Hg NMR (by INDOR) has been used to determine stability constants for $MeHgCl_2^-$ at 26° (0.31 l/mole) and for $MeHgBr_2^-$ at 26° (0.94 l/mole) and at 60° (0.70 l/mole) in ethanol solution (192).

Finally, of interest are 1:1 charge-transfer complexes between π-anilinechromium tricarbonyls and mercuric chloride in which the donor site apparently is the chromium atom (193):



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

10. STRUCTURAL, SPECTROSCOPIC AND PHYSICAL STUDIES

A. Structural Studies

The structural chemistry of organomercury compounds has been reviewed (4). X-ray diffraction studies of organomercurials and of some inorganic mercury compounds relevant to organomercury chemistry have been reported.

Bis(1,3-tetraphenylbutadienemercuric cyanide)mercury, $Hg(\underset{R}{C}=\underset{R}{C}-\underset{R}{C}=\underset{R}{C}-HgCN)_2$ (R = Ph) (Fig. 8) (194). The central C-Hg-C bond angle is 177°.

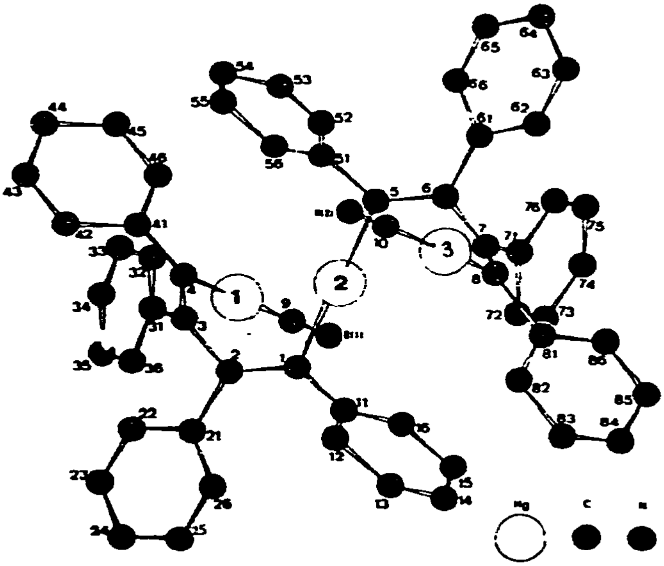
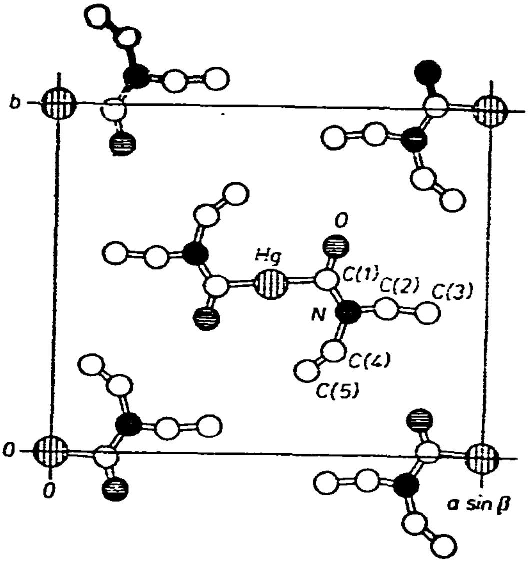


Figure 8. The structure of bis(1,3-tetraphenylbutadienemercuric cyanide)-mercury. (from M. Peteau-Borsdenghien, J. Meunier-Piret and M. Van Meerssche, Cryst. Struct. Comm., 4 (1975) 383)

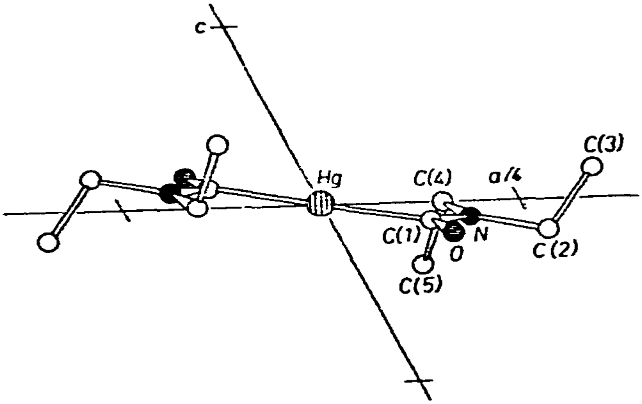
Bis(diethylcarbamoyl)mercury, $Hg(\underset{\overset{\|}{O}}{C}NEt_2)_2$ (Fig. 9) (195). The Hg-C distance is 2.13(2) Å.

There is no intermolecular coordination involving either Hg--N or Hg--O interactions.

1-Methyl-4-thiouracil-p-mercuribenzoic acid (Fig. 10) (196). Hydrogen-bonded dimers [(carboxyl)O-H---O(uracil)] are present. The S-Hg-C group is linear.



Projection of the unit cell of the bis(diethylcarbamoyl)mercury crystal along the c axis



Projection of one molecule of bis(diethylcarbamoyl)mercury along the −b axis

Figure 9. The structure of bis(diethylcarbamoyl)mercury (from K. Toman and G.G. Hess, Z. Krist., 142 (1975) 35)

Methyl(L-cysteinato)mercury (Fig. 11) (197). The amino acid ligand is coordinated to mercury via a deprotonated sulfhydryl group. In addition, there is weak intramolecular Hg---O interaction to the carboxylate group.

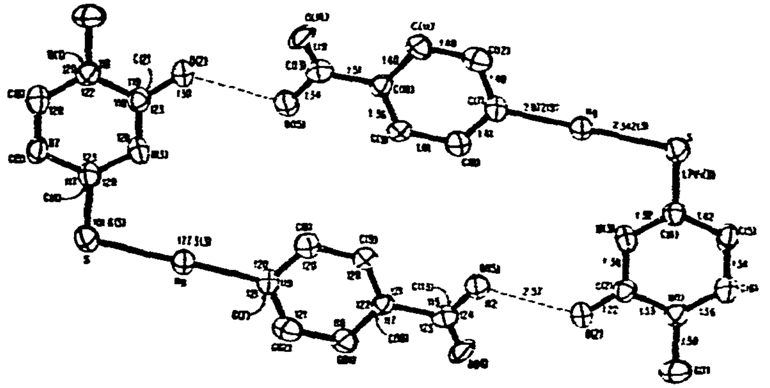


Figure 10. The structure of 1-methyl-4-thiouracil-p-mercuribenzoic acid (from S. W. Hawkinson, B. C. Pal and J. R. Einstein, Cryst. Struct. Comm., 4 (1975) 557)

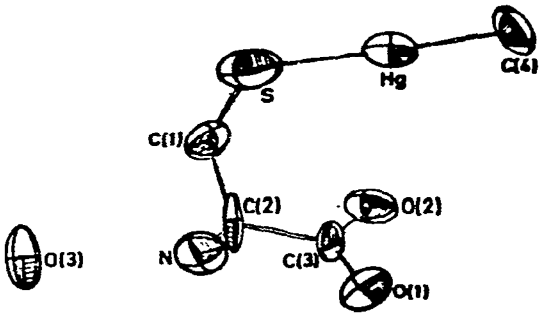


Figure 11. Structure of methyl(L-cysteinato)mercury monohydrate. (O(3) is the oxygen atom of the molecule of water of crystallization). (from N. J. Taylor, Y. S. Wong, P. C. Chieh and A. J. Carty, J. Chem. Soc. Dalton Trans. (1975) 438)

n-Propyl- and n-butylmercaptomercuric acetate, RS-Hg-OAc (198). The mercury atoms and the thioalkoxy groups are linked in angular chains with acetate bridges connecting the chains into layers.

B. Spectroscopic Studies

i. Vibrational Spectroscopy

The vibrational spectra of $MeHgCH_2CN$, $MeHgCD_2CN$ and $(MeHg)_3CCN$ have been studied (133), as have the IR spectra of mercury derivatives of arenechromium tricarbonyl complexes (199).

ii. Nuclear Magnetic Resonance Spectroscopy

Two studies of ^{199}Hg chemical shifts as obtained by Fourier Transform NMR have been published. Borzo and Maciel (200) studied organomercuric chlorides and carboxylates. Both classes of compounds showed large solvent and substituent effects. Similar observations were made by Odom and his coworkers (201); some of their data are given in Tables 13 and 14.

A number of papers has dealt with ^{13}C NMR spectroscopy of organomercurials (^{13}C NMR chemical shifts and ^{13}C-^{199}Hg spin-spin coupling constants): of diorganomercurials (202), of neopentylmercury compounds (203), of benzylmercurials and diphenylmercury (204), of selected organomercuric acetates and chlorides with an aim of examining the angular dependence of vicinal ^{13}C-^{199}Hg coupling (205), of a series of dialkyl- and bis(perfluoroalkyl)mercurials in chloroform and in donor solvents (206), of dimethylmercury in a nematic solvent (207).

The study of the angular dependence of vicinal ^{13}C-^{199}Hg coupling merits special discussion. From such data for appropriately chosen mercurials which are listed below, the following dihedral angle- coupling

(Continued on p. 283)

Table 13. Mercury-199 Chemical Shifts[a] (from Ref. 201)

Compound	Concentration	Solvent	Shift(ppm)
$Hg(CH_3)_2$	neat		0
$Hg(CH_3)_2$	20% mole	pyridine	-82[b]
$Hg(CH_3)_2$	1.00 M	DMSO	-108.8
$Hg(C_2H_5)_2$	neat		-280[b]
$Hg(C_2H_5)_2$	neat		-288.6
$Hg(C_2H_5)_2$	2 M	CCl_4	-304
$Hg(C_2H_5)_2$	neat		-330
$Hg(C_2H_5)_2$	sat. (~1 M)	DMSO	-364.7
$Hg(CHCH_2)_2$	20%	TMS	-621
$Hg(CHCH_2)_2$	neat		-641.9
$Hg(CHCH_2)_2$	2 M	CH_2Cl_2	-648
$Hg(CHCH_2)_2$	1.0 M	DMSO	-716.5
$Hg(C_6H_5)_2$	1.0 M	CH_2Cl_2	-742
$Hg(CH_3)(Cl)$	0.52 M	pyridine	-785.3[c]
$Hg(C_6H_5)_2$	1.00 M	DMSO	-808.5
$Hg(CH_3)(Cl)$	0.51 M	DMSO	-847.9
$Hg(CH_3)(Cl)$	1.00 M	DMSO	-847.9
$Hg(CH_3)(Br)$	0.50 M	pyridine	-899.3[c]
$Hg(C_2H_5)(Cl)$	1.00 M	DMSO	-910.8
$Hg(CH_3)(Br)$	1.00 M	DMSO	-959.1
$Hg(CH_3)(Br)$	0.49 M	DMSO	-965.3
$Hg(CH_3)(I)$	0.50 M	pyridine	-1102.5[c]
$Hg(CH_3)(I)$	1.00 M	DMSO	-1142.6

Table 13. Continued

$Hg(p\text{-}CH_2C_6H_4)(Cl)$	1.00 M	DMSO	-1151.0
$Hg(p\text{-}CH_3C_6H_4)(Cl)$			-1152
$Hg(CH_3)(I)$	0.49 M	DMSO	-1152.8[c]
$Hg(C_6H_{11})(OCOCH_2CH_2CH_3)$	0.50 M	DMSO	-1175.6
$Hg(C_6H_5)(Cl)$			-1180
$Hg(C_6H_5)(Cl)$	0.50 M	DMSO	-1186.6
$Hg(C_6H_5)(CBr_2Cl))$	1.00 M	DMSO	-1186.9
$Hg(C_6H_5)(COOC_6H_5)$	1.00 M	DMSO	-1428.3
$Hg(C_6H_5)(OCOCH_3)$	1.00 M	DMSO	-1436.7
$Hg_2(C_6H_5)_2(o\text{-}(COO)_2C_6H_4)$	0.50 M	DMSO	-1443.0
$HgCl_2$	0.25 M	C_2H_5OH	-1498.4[c]
$HgCl_2$	1.00 M	DMSO	-1501.6
$HgCl_2$	1.39 M	C_2H_5OH	-1515.5[c]
$Hg(ClO_4)_2$ (3.78 g in 3 ml 1.0 M-$HClO_4$)			-2284.0

---

[a] Referenced to external neat dimethylmercury: + sign denotes resonances to lower shielding.

[b] Referenced to neat dimethylmercury using the conversion $Hg(NO_3)_2$ (saturated aqueous solution) is +2460 ppm from neat dimethylmercury.

[c] Referenced to neat dimethylmercury using the conversion $(C_6H_5CH_2CH_2)_2Hg$ is +310.6 ppm from neat dimethylmercury: obtained by assuming CH_3HgCl(0.51 M DMSO)=CH_3HgCl(1.00 M DMSO).

Table 14. Influence of Solvents on the ^{199} Chemical Shifts of Dimethylmercury (1.00 M Solutions) (Ref. 201)

Solvent	Chemical shift (ppm)[a]
1. Dimethyl sulfoxide	-108.2
2. N,N-dimethylformamide	-94.6
3. Pyridine	-94.0
4. 1,4-dioxane	-91.0
5. Diglyme	-81.3
6. Acetonitrile	-78.3
7. Tetrahydrofuran	-75.9
8. Acetone	-71.2
9. Methyl formate	-66.8
10. Ethyl acetate	-57.5
11. Benzene	-50.4
12. Toluene	-50.1
13. Mixed xylene	-48.6
14. Methylene chloride	-42.1
15. Diethyl ether	-28.8
16. Chloroform	-28.2
17. Carbon tetrachloride	-11.2
18. Neat dimethylmercury	0.0
19. Cyclohexane	+0.8
20. Cyclopentane	+2.2
21. Hexane	+5.3

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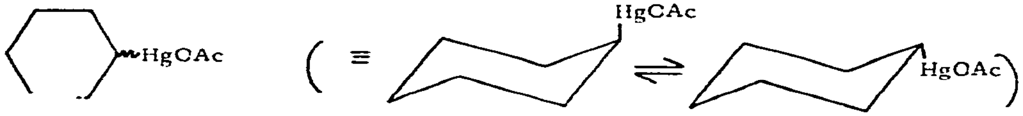
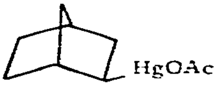
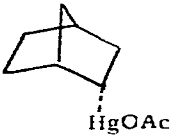
[a] With respect to external neat dimethylmercury; + sign denotes resonances to a lower shielding.







constant combinations were observed in $CDCl_3$ solution:

θ:	35°	60°	85°	120°	160°	170°	180°
J(Hz):	159	78 72	9	93	244	276	268 275 282

These data give a Karplus-type curve and this variation of J with θ should be useful in structural studies of alkylmercurials.

A study of the ^{13}C NMR spectra of the fluxional molecules $(\eta^1\text{-}C_5H_5)HgCl$ and $(\eta^1\text{-}C_9H_7)_2Hg$ over the temperature range -122° to 22° served to establish that the fluxional process in the former involves rearrangement via 1,2 shifts with an activation energy of 7.7 ± 0.7 kcal/mol (208). ^{13}C NMR spectroscopy was used to examine the occurence of σ-π conjugation in a number of α-chloromercuriketones (209).

The ^{14}N NMR spectrum of methylmercuric nitrate has been reported (210).

iii. Nuclear Quadrupole Resonance Spectroscopy

The ^{35}Cl NQR spectra of a number of chlorinated mercurials (trans-ClCH=CHHgCl, CCl_3HgR (R = Cl, Br, CCl_3, Ph), various C_5Cl_5-Hg derivatives) have been measured and discussed in terms of intermolecular Cl--Hg interactions and, in the case of pentachlorocyclopentadienylmercury compounds, Hg-C σ-π conjugation (211, 212).

iv. Photoelectron Spectroscopy

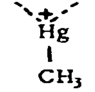
Photoelectron spectra of CF_3HgX (X = I, N_3, NCO, NO_3) and of $Hg(SCF_3)_2$ have been obtained (213). Mercury 5d electrons participate slightly in bonding. Consideration of the photoelectron spectrum of benzylmercuric chloride led to the conclusion that this molecule in the gas phase exists in a conformation in which the C-Hg bond can interact with the π system of the benzene ring, i.e., the C_{Ph}=C_{Ph}-C-Hg dihedral angle is 90° or nearly 90° (214). Extended Hückel calculations on benzylmercuric bromide also led to this result (215).

v. Other Spectroscopy

The microwave spectra of methylmercuric chloride, bromide and iodide have been reported. C-Hg and X-Hg bond distances were calculated from the data obtained (216).

The charge-transfer spectrum of $Me_2Hg\cdot(NC)_2C=C(CN)_2$ in chloroform showed a CT band at 24,100 cm^{-1} (217).

Ion cyclotron resonance studies of the gas phase reaction of $MeHg^+$ (via Me_2Hg) and allene provided evidence for the formation of a mercurinium ion, 39 (218).



39

Fluorescence quenching of anthracene by dimethyl- and diphenylmercury has been observed (219).

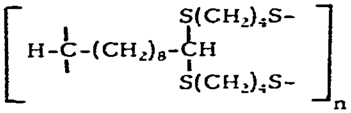
C. Thermochemistry

The heats of formation of $(EtHg)_2O$ and $EtHgOOCMe_2Ph$ have been determined (220). Valence bond calculations of the Hg-C and C-Cl bond energies in *cis*- and *trans*-ClCH=CHHgCl have been carried out (221). These bonds were calculated to be significantly stronger in the *cis* than in the *trans* isomer.

11. ANALYTICAL ASPECTS OF ORGANOMERCURY CHEMISTRY

Isothiocyanatopentaaquochromium(III) forms polynuclear species with mercuric, mercurous and methylmercuric ions, e.g., $(H_2O)_5CrNCSHg^{4+}$, $(H_2O)_5CrNCSHgCH_3^{3+}$, etc. This provides the basis for the separation and identification of these mercury species in aqueous solution in conjunction with cation exchange techniques in the 1-100 ppb concentration range (222).

An aniline-sulfur resin was found to be an effective matrix for selective preconcentration of mercuric nitrate and methylmercuric chloride from aqueous solutions at pH 6-7 at ppm levels prior to their determination by neutron activation analysis (223). At pH 0.3, this resin may be used to separate Hg^{2+} from CH_3Hg^+ (224). Methylmercuric chloride and inorganic mercury(II) also may be extracted from aqueous solution over a wide pH range for Hg concentrations below 10 ppm using diphenylthiocarbazone-treated polyurethane foams (225). Elution with acetone frees the mercury species. Of interest also is a new glutaraldehyde-butanedithiol polymer which binds Hg(II) with high selectivity (226):



$$\left[H-\overset{|}{\underset{|}{C}}-(CH_2)_8-\overset{S(CH_2)_4S-}{\underset{S(CH_2)_4S-}{\overset{|}{\underset{|}{C}}H}} \right]_n$$

Multistage air samplers for the collection and separation of metallic mercury, inorganic mercury and organomercury species in air have been developed (227, 228).

Also reported have been GC-mass spectral analysis of alkylmercury compounds (229), the adsorption of methylmercuric chloride on humic acid and humic acid chars (230), GC analysis of ppb levels of methylmercuric chloride by foam separation (231), the thin layer chromatographic analysis of methoxymercuration products of mono-unsaturated long chain esters (232) and the determination of higher terminal olefins by spectrophotometric analysis of their methoxymercuration products by the diphenyl carbazone method (233).

REFERENCES

1. M. H. Abraham, in "Comprehensive Chemical Kinetics", Vol. 12, "Electrophilic Substitution at a Saturated Carbon Atom", C. H. Bamford and C. F. H. Tipper, ed., Elsevier, 1973, xiii + 256 pp.
2. D. R. M. Walton, J. Organometal. Chem., 90 (1975) C20
3. D. Seyferth in "Carbenes", Vol. 2, R. A. Moss and M. Jones, Jr., ed., Wiley-Interscience, New York, 1975, pp. 101-158.
4. L. G. Kuzmina, N. G. Bokii and Yu. T. Struchkov, Usp. Khim., 44 (1975) 134; Russ. Chem. Rev., 44 (1975) 73
5. G. A. Tedoradze, J. Organometal. Chem., 88 (1975) 1
6. A. Lattes, Khim. Geterotsikl. Soed. (1975) 7

7. S. F. Zhil'tsov and O. N. Druzhkov, Tr. Khim. Khim. Tekhnol. (1974) 13; Chem. Abstr., 83 (1975) 179165w

8. O. A. Reutov and K. P. Butin, J. Organometal. Chem., 99 (1975) 171

9. A. A. Morton, Chem. Rev., 75 (1975) 767

10. H. L. Elbe and G. Köbrich, Tetrahedron Lett. (1974) 2557

11. D. Seyferth, R. L. Lambert, Jr. and M. Massol, J. Organometal. Chem., 88 (1975) 255

12. B. I. Martynov, S. R. Sterlin and B. L. Dyatkin, Izv. Akad. Nauk SSSR, Ser. Khim. (1974) 1642

13. A. N. Nesmeyanov, N. N. Sedova, V. A. Saznova, I. F. Leshcheva and I. S. Rogozhin, Dokl. Akad. Nauk SSSR, 218 (1974) 356

14. K. P. Butin, V. V. Strelets, I. F. Gunkin, I. P. Beletskaya and O. A. Reutov, J. Organometal. Chem., 85 (1975) 123

15. A. M. Devine, P. A. Griffin, R. N. Haszeldine, M. J. Newlands and A. E. Tipping, J. Chem. Soc., Dalton Trans. (1975) 1434

16. A. M. Devine, R. N. Haszeldine and A. E. Tipping, J. Chem. Soc., Dalton Trans. (1975) 1837

17. E. D. Babich, M. V. Pozdnyakova, N. V. Ushakov, V. M. Vdovin and N. S. Nametkin, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 1600

18. A. N. Nesmeyanov, T. P. Tolstaya, V. V. Korol'kov and A. N. Yarkevich, Dokl. Akad. Nauk SSSR, 221 (1975) 1337

19. J. H. Espenson, W. R. Bushey and M. E. Chmielewski, Inorg. Chem., 14 (1975) 1302

20. H. Yamamoto, T. Yokoyama, J.-L. Chen and T. Kwan, Bull. Chem. Soc. Japan, 48 (1975) 844

21. G. B. Deacon, G. J. Farquharson and J. M. Miller, J. Organometal. Chem., 94 (1975) C33

22. G. B. Deacon, J. M. Miller and B. S. F. Taylor, Aust. J. Chem., 28 (1975) 1499

23. R. J. Bertino, B. A. W. Coller, G. B. Deacon and I. K. Johnson, J. Fluorine Chem., 5 (1975) 335

24. Yu. A. Ol'dekop, N. A. Maier, Yu. D. But'ko and I. A. Shingel, Vestsi Akad. Navuk B.SSR, Ser. Khim. Navuk (1974) (6) 63; Chem. Abstr., 83 (1975) 112148d

25. T. N. Shatkina, K. S. Mazel' and O. A. Reutov, Dokl. Akad. Nauk SSSR, 219 (1974) 1392

26. T. N. Shatkina, A. N. Lovtsova, T. I. Pekhk, E. T. Kippmaa and O. A. Reutov, Dokl. Akad. Nauk SSSR, 220 (1975) 139

27. A. N. Lovtsova, T. N. Shatkina and O. A. Reutov, Dokl. Akad. Nauk SSSR, 220 (1975) 380

28. R. Eujen and R. J. Lagow, Inorg. Chem., 14 (1975) 3128

29. R. J. Lagow, L. L. Gerchman, R. A. Jacob and J. A. Morrison, J. Amer. Chem. Soc., 97 (1975) 518

30. J. D. McCullough, Inorg. Chem., 14 (1975) 2285

31. H. Akagi, Y. Fujita and E. Takabatake, Chem. Lett. (1975) 171

32. I. L. Knunyants, N. P. Aktaev, N. P. Semenov and G. A. Sokol'skii, Dokl. Akad. Nauk SSSR, 219 (1974) 113

33. O. S. Morozov, L. M. Dyagileva, N. N. Vyshinskii and Yu. A. Aleksandrov, Zh. Obshch. Khim., 45 (1975) 246

34. N. Garti and Y. Halpern, J. Appl. Chem. Biotechnol., 25 (1975) 249

35. Y. Halpern and N. Garti, J. Organometal. Chem., 88 (1975) 315

36. Y. Halpern and N. Garti, J. Organometal. Chem., 92 (1975) 291

37. Y. Halpern and N. Garti, I & EC Prod. Res. Dev., 14 (1975) 71

38. J. A. Todhunter and D. L. Currell, J. Org. Chem., 40 (1975) 1362

39. B. Bockrath and L. M. Dorfman, J. Amer. Chem. Soc., 97 (1975) 3307

40. J. Hartmann and M. Schlosser, Synth. (1975) 329

41. B. De Groof, M. Van Beylen and M. Szwarc, Macromol., 8 (1975) 396

42. L. L. Ivanov, S. Ya. Zavizion and L. I. Zakharkin, Zh. Obshch. Khim., 45 (1975) 1060

43. S. B. Miller, B. L. Jelus and T. B. Brill, J. Organometal. Chem., 96 (1975) 1

44. G. S. Burlachenko, Yu. I. Baukov, T. G. Dzherayan and I. F. Lutsenko, Zh. Obshch. Khim., 45 (1975) 81

45. A. N. Nesmeyanov, T. P. Tolstaya and V. V. Korol'kov, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 652

46. M. Malnar, Bull. Sci., Cons. Acad. Sci. Arts RSF Yougoslavie, Sect. A, 19 (1974) 65; Chem. Abstr., 81 (1974) 49767s

47. J. D. McCullough, Inorg. Chem., 14 (1975) 2285

48. A. Z. Rubezhov, A. S. Ivanov and S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 1196

49. A. Z. Rubezhov, A. S. Ivanov and S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim. (1974) 2651

50. A. Z. Rubezhov, A. S. Ivanov and S. P. Gubin, Izv. Akad. Nauk SSSR, Ser. Khim. (1974) 1902

51. V. I. Sokolov, V. V. Bashilov and O. A. Reutov, J. Organometal. Chem., 97 (1975) 299

52. V. I. Sokolov, L. L. Troistskaya and O. A. Reutov, J. Organometal. Chem., 93 (1975) C11

53. J.-E. Bäckvall and B. Åkermark, J. Chem. Soc., Chem. Comm. (1975) 82

54. J. K. Stille and P. K. Wong, J. Org. Chem., 40 (1975) 335

55. A. J. Bloodworth and I. M. Griffin, J. Chem. Soc., Perkin Trans. I (1975) 695

56. J. T. Slama, H. W. Smith, C. G. Willson and H. Rapoport, J. Amer. Chem. Soc., 97 (1975) 6556

57. R. A. Bekker, G. G. Melikyan, B. L. Dyatkin and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 221 (1975) 1331

58. E. M. Gaydou, A. Guillemonat and M. T. Bendayan, Bull. Soc. Chim. France (1975) 805

59. W. C. Baird, Jr. and J. H. Surridge, J. Org. Chem., 40 (1975) 1364

60. R. C. Larock, J. Org. Chem., 40 (1975) 3237

61. T. Izumi, T. Takeda and A. Kasahara, Yamagata Daigaku Kiyo Kogaku, 13 (1974) 193; Chem. Abstr., 81 (1974) 120756v

62. A. Kasahara, T. Izumi, G. Saito and T. Takeda, Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku, 22 (1973) 95: Chem. Abstr., 81 (1974) 135859e

63. T. Takagi, T. Okamoto, Y. Sakakibara, A. Ohno, S. Oka and N. Hayama, Chem. Lett. (1975) 951

64. T. Izumi and A. Kasahara, Bull. Chem. Soc. Japan, 48 (1975) 1955

65. W. Ried, W. Merkel and S.-W. Park, Justus Liebigs Ann. Chem. (1975) 79

66. H. Sawai and T. Takizawa, J. Organometal. Chem., 94 (1975) 333

67. E. V. Couch, J. A. Landgrebe and E. T. Castaneda, J. Org. Chem., 40 (1975) 1529

68. T. H. Chan and D. Masruda, Tetrahedron Lett. (1975) 3383

69. R. A. Magarian and E. J. Benjamin, J. Pharm. Sci., 64 (1975) 1626

70. C. W. Jefford, W. D. Graham and U. Burger, Tetrahedron Lett. (1975) 4717

71. R. A. Moss and C. B. Mallon, J. Amer. Chem. Soc., 97 (1975) 344

71a. B. F. Bonini, A. Cappelli, G. Maccagnani and G. Mazzanti, Gazz. Chim. Ital., 105 (1975) 827

72. D. Seyferth and C. K. Haas, J. Org. Chem., 40 (1975) 1620

73. D. Seyferth, G. J. Murphy and R. A. Woodruff, J. Organometal. Chem., 92 (1975) 7

74. A. K. Mal'tsev, N. D. Kagramanov and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim. (1974) 1993

75. N. D. Kagramanov, A. K. Mal'tsev and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim. (1974) 2146

76 G A. Olah and S. H. Yu, J. Org. Chem., 40 (1975) 3638

77. H. Hodjat-Kachani, A. Lattes, J. J. Perie and J. Roussel, J. Organometal. Chem., 96 (1975) 175

78. C. Georgoulis and J.-M. Valery, Bull. Soc. Chim. France II (1975) 1431

79. B. Giese, Chem. Ber., 108 (1975) 2998

80. B. Giese, Chem. Ber., 108 (1975) 2978

81. N. Takaishi, Y. Fujikura and Y. Inamoto, J. Org. Chem., 40 (1975) 3767

82. G. Mehta and P. N. Pandey, J. Org. Chem., 40 (1975) 3631

83. N. A. Keiko, T. P. Musorina, A. A. Tatrinova and M. G. Voronkov, Izv. Akad. Nauk SSSR. Ser. Khim. (1975) 1617

84. A. T. do Amaral, O. A. El Seoud and L. do Amaral, J. Org. Chem., 40 (1975) 2534

85. B. Floris and G. Illuminati, Coord. Chem. Rev., 16 (1975) 107

86. G. R. Krow and J. Reilly, J. Org. Chem., 40 (1975) 136

87. K. M. Nicholas, J. Amer. Chem. Soc., 97 (1975) 3254

88. A. Banaszek, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 22 (1975) 1045

89. S. Czernecki, C. Georgoulis and C. Provelenghiou , Tetrahedron Lett. (1975) 2623

90. S. C. Misra and G. Chandra, Ind. J. Chem., 13 (1975) 1239

91. R. G. Agrawal, G. K. Trivedi and S. C. Bhattacharyya, Ind. J. Chem., 13 (1975) 876

92. M. Julia, Fr. Demande 2,224,477 (1974); Chem. Abstr., 83 (1975) 10407r

93. M. Julia, J.-D. Fourneron and C. Thal, Anal. Quim., 70 (1975) 888

94. V. A. Nikanorov, V. I. Rozenberg, R. I. Gorbacheva, Yu. G. Bundel' and O. A. Reutov, J. Organometal. Chem., 101 (1975) 259

95. V. I. Rozenberg, V. A. Nikanorov, V. I. Salikova, Yu. G. Bundel' and O. A. Reutov, J. Organometal. Chem., 102 (1975) 7; Dokl. Akad. Nauk SSSR, 223 (1975) 879

96. A. J. Bloodworth and I. M. Griffin, J. Chem. Soc., Perkin Trans. I (1975) 195

97. A. J. Bloodworth and I. M. Griffin, J. Chem. Soc., Perkin Trans. II (1975) 531

98. I. Torrini and A. Romeo, Tetrahedron Lett. (1975) 2605

99. A. Lethbridge, R. O. C. Norman, C. B. Thomas and W. J. E. Parr, J. Chem. Soc., Perkin I (1975) 231

100. A. Lethbridge, R. O. C. Norman and T. C. Barry, J. Chem. Soc., Perkin I (1974) 1929

101. H. R. Rogers, J. X. McDermott and G. M. Whitesides, J. Org. Chem., 40 (1975) 3577

102. I. P. Beletskaya and A. V. Ryabtsev, Vysokomol. Soed. B, 17 (1975) 75; Chem. Abstr., 83 (1975) 193797k

103. M. Kosaki, S. Shinoda and Y. Saito, Bull. Chem. Soc. Japan, 48 (1975) 3745

104. S. Shinoda and Y. Saito, J. Organometal. Chem., 90 (1975) 1

105. R. D. Bach and R. N. Brummel, J. Amer. Chem. Soc., 97 (1975) 453

106. B. M. Mikhailov, L. S. Vasil'ev, V. V. Veselovskii and V. G. Kiselev, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 725

107. N. S. Kozlov and G. P. Korotyshova, Vestsi Akad. Navuk B. SSR, Ser. Khim. Navuk (1974) 52; Chem. Abstr., 82 (1975) 43558y

108. M. A. Kazankova, T. Ya. Satina and I. F. Lutsenko, Zh. Obshch. Khim., 45 (1975) 712

109. M. A. Kazankova, T. Ya. Satina and I. F. Lutsenko, Zh. Obshch. Khim., 45 (1975) 1195

110. S. Uemura, H. Miyoshi, K. Sohma and M. Okano, J. Chem. Soc., Chem. Comm. (1975) 548

111. J. Barluenga and F. Aznar, Synthesis (1975) 704

111a. B. S. Thyagarajan, K. C. Majumdar and D. K. Bates, J. Heterocyclic Chem., 12 (1975) 59

112. Yu. S. Shabarov, S. G. Bandaev and L. D. Sychkova, Zh. Org. Khim., 11 (1975) 1218

113. Yu. S. Shabarov, L. D. Sychkova and S. G. Bandaev, J. Organometal. Chem., 99 (1975) 213

114. Yu. S. Shabarov, L. D. Sychkova, S. G. Bandaev and O. A. Subbotin Zh. Obshch. Khim., 45 (1975) 2300

115. Yu. S. Shabarov, S. S. Mochalov, L. M. Simakova and T. S. Oretskaya, Zh. Org. Khim., 11 (1975) 2049

116. I. I. Bardyshev, E. F. Buinova, G. V. Deshchits and V. V. Khmel'nitskaya, Zh. Org. Khim., 11 (1975) 1424

117. A. Balsamo, C. Battistini, P. Crotti, B. Macchia and F. Macchia, J. Org. Chem., 40 (1975) 3233

118. E. Müller, Chem. Ber., 108 (1975) 1394

119. E. Müller, Chem. Ber., 108 (1975) 1401

119a. S. V. Zotova and N. M. Abramova, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 1912

120. R. N. Butler and W. B. King, Chem. Ind. (London) (1975) 647

121. S. Mansy and R. S. Tobias, Inorg. Chem., 14 (1975) 287

122. H. Alper and W. G. Root, J. Amer. Chem. Soc., 97 (1975) 4251

123. P. Yates, F. Z. Garneau and J. P. Lokensgard, Tetrahedron 31 (1975) 1979

124. T. B. Patrick and G. H. Kovitch, J. Org. Chem., 40 (1975) 1527

125. W. A. Hermann, J. Organometal. Chem., 97 (1975) 1

126. F. Bonati and G. Minghetti, Synth. React. Inorg. Metal-org. Chem., 5 (1975) 135

127. L. E. McCandlish and J. W. Macklin, J. Organometal. Chem., 99 (1975) 31

128. K. Dietrich, H. Musso and R. Allmann, J. Organometal. Chem., 93 (1975) 15

129. R. H. Fish, R. E. Lundlin and C. G. Salentine, J. Organometal. Chem., 84 (1975) 281

130. G. Engelhardt, B. Schuknecht and E. Uhlemann, Z. Chem., 15 (1975) 367

130a. K. Dietrich and H. Musso, Angew. Chem., 87 (1975) 384

131. I. F. Lutsenko, Yu. I. Baukov and E. P. Kramarova, Zh. Obshch. Khim., 44 (1974) 2361

132. Z. S. Novikova, N. P. Sadovnikov, S. N. Zdorova and I. F. Lutsenko, Zh. Obshch. Khim., 44 (1974) 2233

133. F. Weller, Z. anorg. allg. Chem., 415 (1975) 233

134. G. Minghetti, F. Bonati and M. Massobrio, Inorg. Chem., 14 (1975) 1974

134a. E. T. Weleski, Jr., J. L. Silver, M. D. Jansson and J. L. Burmeister, J. Organometal. Chem., 102 (1975) 365

135. S. F. Zhil'tsov, L. I. Kachaeva, L. F. Kudryavtsev, V. N. Kashaeva, G. G. Petukhov and Yu. A. Kaplin, Zh. Obshch. Khim., 44 (1974) 2496

136. S. F. Zhil'tsov, L. I. Kachaeva and O. N. Druzhkov, Zh. Obshch. Khim., 45 (1975) 1793

137. R. Vaidyanathaswamy and D. Devaprabhakara, Ind. J. Chem., 13 (1975) 287

138. J. Barluenga, J. M. Concellon and G. Asensio, Synthesis (1975) 467

139. V. I. Bregadze, D. N. Sadzhaya and O. Yu. Ckhlobystin, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 395

140. A. Macias and T. Garcia, Rev. CENIC, Cienc. Fis., 5 (1974) 271; Chem. Abstr., 82 (1975) 111265c

141. I. P. Beletskaya, Y. A. Artamkina and O. A. Reutov, J. Organometal. Chem., 99 (1975) 343

142. S. F. Zhil'tsov, V. I. Shcherbakov and O. N. Druzhkov, Tr. Khim. Khim. Tekhnol. (1974) 62; Chem. Abstr., 83 (1975) 193469e

143. E. V. Uglova, V. D. Makhaev and O. A. Reutov, Zh. Org. Khim., 11 (1975) 3

144. V. A. Nikanorov, V. I. Rozenberg, G. V. Gavrilenko, Yu. G. Bundel' and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 1910

145. N. A. Nikanorov, V. I. Rozenberg, G. V. Gavrilova, Yu. G. Bundel' and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 1675

146. M. N. Bochkarev, L. P. Maiorova, N. S. Vyazankin and G. A. Razuvaev, J. Organometal. Chem., 82 (1975) 65

147. A. L. Bluhm and J. Weinstein, Spectroscopy Lett., 8 (1975) 43

148. T. N. Huckerby, P. H. Lindsay, F. G. Thorpe and J. C. Podesta, Tetrahedron, 31 (1975) 277

149. I. P. Beletskaya, K. P. Butin, V. N. Shishkin, V. F. Gomzyakov, I. F. Gun'kin and O. A. Reutov, Zh. Org. Khim., 10 (1974) 2009

150. K. P. Butin, V. N. Shishkin, I. P. Beletskaya and O. A. Reutov, Dokl. Akad. Nauk SSSR, 218 (1974) 371

151. M. H. Abraham, P. L. Grellier and M. J. Hogarth, J. Chem. Soc., Perkin Trans. II (1974) 1613

152. D. L. Rabenstein, C. A. Evans, M. C. Tourangeau and M. T. Fairhurst, Anal. Chem., 47 (1975) 338

153. R. D. Bach and A. T. Weibel, J. Amer. Chem. Soc., 97 (1975) 2575

154. D. De Vos, D. C. Van Beelen, H. O. Van der Kooi and J. Wolters, Rec. Trav. Chim., 94 (1975) 100

155. L. M. Epshtein, L. D. Ashkinadze, Z. F. Dau, D. N. Kravtsov and L. A. Kazitsyna, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 153

156. V. I. Minkin, L. P. Olekhnovich, M. I. Knyazhanskii, I. E. Mikhailov and A. E. Lyubarskaya, Zh. Org. Khim., 10 (1974) 817

157. V. I. Buzulukov, V. P. Maslennikov, V. F. Khodalev and Yu. A. Aleksandrov, Zh. Obshch. Khim., 44 (1974) 2549

158. V. I. Buzulukov, V. P. Maslennikov, V. P. Sergeeva and Yu. A. Aleksandrov, Zh. Obshch. Khim., 44 (1974) 2790

159. V. I. Buzulukov, V. P. Maslennikov and Yu. A. Aleksandrov, Tr. Khim. Khim. Tekhnol. (1974) No. 4, 68; Chem. Abstr., 83 (1975) 192288h

160. G. Guanti, M. Novi, C. Dell'Erba and G. Leandri, J. Chem. Soc. Perkin Trans. II (1975) 1490

161. D. L. Rabenstein and M. T. Fairhurst, J. Amer. Chem. Soc., 97 (1975) 2086

162. H. Leimeister and K. Dehnicke, Z. anorg. allg. Chem., 415 (1975) 115

163. I. Haiduc and E. Veres, Synth. React. Inorg. Metal-org. Chem., 5 (1975) 115

164. N. N. Greenwood, B. S. Thomas and D. W. Waite, J. Chem. Soc. Dalton Trans. (1975) 299

165. P. Clare and F. Glockling, Inorg. Chim. Acta, 14 (1975) L12

166. R. N. Haszeldine, D. J. Rogers and A. E. Tipping, J. Chem. Soc. Dalton Trans. (1975) 2225

167. A. Haas, B. Koch and N. Welcman, Chem. Ztg., 98 (1974) 511

168. N. Watanabe, M. Okano and S. Uemura, Bull. Chem. Soc. Japan, 47 (1974) 2745

169. M. J. Albright, T. F. Schaaf, W. M. Butler, A. K. Hovland, M. D. Glick and J. P. Oliver, J. Amer. Chem. Soc., 97 (1975) 6261

170. S. Cradock, E. A. V. Ebsworth, N. S. Hosmane and K. M. Mackay, Angew. Chem., 87 (1975) 207

171. T. F. Schaaf, R. R. Kao and J. P. Oliver, Inorg. Chem., 14 (1975) 2288

172. O. A. Kruglaya, L. I. Belousova, B. V. Fedot'ev and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 975

173. M. N. Bochkarev, G. A. Razuvaev and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 1820

174. M. Lehnig, F. Werner and W. P. Neumann, J. Organometal. Chem., 97 (1975) 375

175. F. Werner, W. P. Neumann and H. P. Becker, J. Organometal. Chem., 97 (1975) 389

176. W. P. Neumann, B. Schroeder and M. Ziebarth, Justus Liebigs Ann. Chem. (1975) 2279

177. S. V. Ponomarev, H. P. Becker, W. P. Neumann and B. Schroeder, Justus Liebigs Ann. Chem., (1975) 1895

178. C. Eaborn, R. A. Jackson and M. T. Rahman, J. Organometal. Chem., 85 (1975) 15

179. O. A. Kruglaya, I. B. Fedot'eva, B. V. Fedot'ev and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1975) 199

180. E. N. Gladyshev, E. A. Fedorova, L. O. Yuntila, G. A. Razuvaev and N. S. Vyazankin, J. Organometal. Chem., 96 (1975) 169

181. E. N. Gladyshev, E. A. Fedorova, G. A. Razuvaev, L. O. Yntila and N. S. Vyazankin, J. Organometal. Chem., 97 (1975) 25

182. B. I. Petrov, G. S. Kalinina and Yu. A. Sorokin, Zh. Obshch. Khim., 45 (1975) 1905

183. G. A. Razuvaev, V. N. Latyaeva, L. I. Vishinskaya, V. T. Bytchkov and G. A. Vasil'eva, J. Organometal. Chem., 87 (1975) 93

184. T. N. Mitchell, J. Organometal. Chem., 92 (1975) 311

185. D. C. Williams and P. R. Wells, J. Organometal. Chem., 85 (1975) 335, 347

186. A. J. Canty, A. Marker and B. M. Gatehouse, J. Organometal. Chem., 88 (1975) C31

187. L. A. Fedorov, Z. A. Stumbrevichyute, B. I. Martynov and B. L. Dyatkin, Zh. Org. Khim., 11 (1975) 489

188. Z. A. Stumbrevichyute, L. A. Fedorov, B. L. Dyatkin and B. I. Martynov, Zh. Org. Khim., 11 (1975) 2002

189. L. M. Epshtein, Z. F. Dau, L. D. Ashkinadze, D. N. Kravtsov and L. A. Kazitsyna, Izv. Akad. Nauk SSSR, Ser. Khim. (1974) 1710

190. M. T. Fairhurst and D. L. Rabenstein, Inorg. Chem., 14 (1975) 1413

191. A. Santosmacias and L. Ballester-Reventos, Anal. Quim., 71 (1975) 831

192. V. Lucchini and P. R. Wells, J. Organometal. Chem., 92 (1975) 283

193. G. K.-I. Magomedov, V. G. Syrkin, A. S. Frenkel' and A. V. Medvedeva, Zh. Obshch. Khim., 44 (1974) 2277

194. M. Peteau-Borsdeughien, J. Meunier-Piret and M. Van Meerssche, Cryst. Struct. Comm., 4 (1975) 383

195. K. Toman and G. G. Hess, Z. Krist., 142 (1975) 35

196. S. W. Hawkinson, B. C. Pal and J. R. Einstein, Cryst. Struct. Comm., 4 (1975) 557

197. N. J. Taylor, Y. S. Wong, P. C. Chieh and A. J. Carty, J. Chem. Soc. Dalton Trans. (1975) 438

198. H. Puff, R. Sievers and G. Elsner, Z. anorg. allg. Chem., 413 (1975) 37

199. N. K. Rudnevskii, N. N. Vyshinskii, I. I. Grinval'd, A. N. Artemov and N. I. Sirotkin, Tr. Khim. Khim. Tekhnol. (1974) No. 4, 130; Chem. Abstr., 83 (1975) 163172k

200. M. Borzo and G. E. Maciel, J. Magn. Resonance, 19 (1975) 279

201. M. A. Sens, N. K. Wilson, P. D. Ellis and J. D. Odom, J. Magn. Resonance, 19 (1975) 323

202. J. Casanova, H. R. Rogers and K. L. Servis, Org. Magn. Resonance, 7 (1975) 57

203. G. Singh, J. Organometal. Chem., 99 (1975) 251

204. W. Adcock, B. D. Gupta, W. Kitching and D. Doddrell, J. Organometal. Chem., 102 (1975) 297

205. W. Kitching, D. Praeger, D. Doddrell, F. A. L. Anet and J. Krane, Tetrahedron Lett. (1975) 759

206. L. A. Fedorov and Z. A. Stumbrevichyute, Zh. Strukt. Khim., 15 (1975) 1063

207. C. Schumann, H. Dreeskamp and K. Hildebrand, J. Magn. Resonance 18 (1975) 97

208. F. A. Cotton, D. L. Hunter and J. D. Jamerson, Inorg. Chim. Acta, 15 (1975) 245

209. A. N. Nesmeyanov, V. A. Blinova, E. I. Fedin, I. I. Kritskaya and and L. A. Fedorov, Dokl. Akad. Nauk SSSR, 220 (1975) 1336

210. K. F. Chew, M. A. Healy, M. I. Khalil, N. Logan and W. Derbyshire, J. Chem. Soc. Dalton Trans. (1975) 1315

211. G. Wulfsberg, R. West and V. N. M. Rao, J. Organometal. Chem., 86 (1975) 303

212. G. Wulfsberg, J. Organometal. Chem., 86 (1975) 321

213. K. Wittel, H. Bock, A. Haas and K. H. Pflegler, J. Electron Spectroscopy, 7 (1975) 365

214. H. Schmidt, A. Schweig and G. Manuel, J. Chem. Soc. Chem. Comm. (1975) 667

215. P. A. Scherr, M. D. Glick, J. H. Siefert and R. D. Bach, J. Amer. Chem. Soc., 97 (1975) 1782

216. C. Walls, D. G. Lister and J. Sheridan, J. Chem. Soc. Faraday Trans. II (1975) 1091

217. V. F. Traven and R. West, Zh. Obshch. Khim., 44 (1974) 1837

218. R. D. Bach, J. Patane and L. Kevan, J. Org. Chem., 40 (1975) 257

219. E. Vander Donckt, M. Lootens, D. Swinnen and C. Haquin, Bull. Soc. Chim. Belg., 84 (1975) 77

220. V. F. Kupriyanov, V. N. A. Alyasov, V. G. Tsvetkov, M. S. Sheiman, V. I. Buzulukov, V. P. Maslennikov and Yu. A. Aleksandrov, Tr. Khim. Khim. Tekhnol. (1974) 80; Chem. Abstr., 82 (1975) 42868n

221. Yu. A. Borisov and A. E. Borisov, Dokl. Akad. Nauk SSSR, 220 (1975) 1325

222. R. J. Baltisberger and C. L. Knudson, Anal. Chem., 47 (1975) 1402

223. H. J. Krämer and B. Neidhart, Radiochem. Radioanal. Lett., 22 (1975) 209

224. H. J. Krämer and B. Neidhart, Radiochem. Radioanal. Lett., 23 (1975) 295

225. A. Chow and D. Buksak, Can. J. Chem., 53 (1975) 1373

226. M. M. Jones, H. D. Coble, T. H. Pratt and R. D. Harbison, J. Inorg. Nucl. Chem., 37 (1975) 2409

227. A. Henriques and J. Isberg, Chem. Scripta, 8 (1975) 173

228. P. E. Trujillo and E. E. Campbell, Anal. Chem., 47 (1975) 1629

229. S. Nishi and Y. Horimoto, Bunsei Kagaku, 24 (1975) 178

230. H. Yoshida, T. Nakamura, T. Miki, S. Arita and M. Nakagawa, Nippon Kagaku Kaishi (1975) 2023

231. T. Hobo, T. Ogura, S. Suzuki and S. Araki, Bunseki Kagaku, 24 (1975) 288

232. D. E. Minnikin and S. Smith, J. Chromatog., 103 (1975) 205

233. M. P. Saxena and K. K. Bhattacharyya, Z. Anal. Chem., 274 (1975) 29