MERCURY

ANNUAL SURVEY COVERING THE YEAR 1971

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CONTENTS

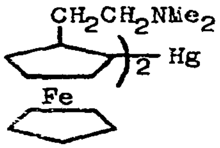
1. REVIEWS

The second part of a long review on the reactions of organomercury compounds by Makarova has appeared (1). Other reviews published in 1971 have included coverage of the following topics:

- Organosilyl- and organogermyl-substituted mercurials (2,3).
- Reactions of phenyl(trihalomethyl)mercury compounds and related compounds with Group IV hydrides and halides (4).
- Reactions of organomercury compounds with polyhalomethanes (5).
- Carbonylation of organomercurials in the presence of stoichiometric or catalytic quantities of cobalt carbonyls (a ketone synthesis) (6).
- The oxymercuration of olefins (7).
- The oxidation of olefins with mercuric salts (8).
- The $S_E1(N)$ mechanism in organomercury chemistry (9).
- Chromatographic and biological aspects of organomercury compounds (10).
- Biological methylation of mercury (mercury pollution of the environment) (11).

2. PREPARATION OF ORGANOMERCURY COMPOUNDS

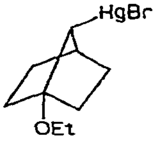
Organic compounds of other metals continue to be useful in the preparation of organomercurials. The synthesis of $\boxed{1}$



$\boxed{1}$

was accomplished via the appropriate ferrocenyl-lithium reagent (12). The action of C_6F_5Li on π-$C_5H_5Fe(CO)_2HgCl$ gave a mixture of $(C_6F_5)_2Hg$ and $Hg\left[Fe(CO)_2C_5H_5\text{-}\pi\right]_2$, rather than the expected $C_6F_5HgFe(CO)_2C_5H_5\text{-}\pi$ (13). However, the latter compound (as well as the related $C_6F_5HgMo(CO)_3C_5H_5\text{-}\pi$ and $C_6F_5Hg\text{-}Mn(CO)_5$) is stable (mp 145-146°) to disproportionation (when prepared by reaction of π-$C_5H_5Fe(CO)_2Na$ with C_6F_5HgBr in THF) (14). The formation of symmetrized products in the C_6F_5Li + π-$C_5H_5Fe(CO)_2HgCl$ reaction is due to the intervention of intermediate anionic intermediates (12).

Grignard reagents were used in the prepartion of $\boxed{2}$ (15) and $\boxed{3}$ (16), and $\boxed{4}$ was prepared by the organolithium procedure (17).



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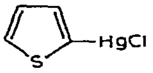

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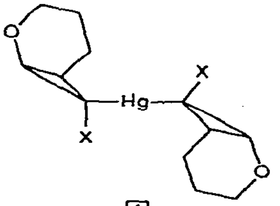


(X=Cl,Br)

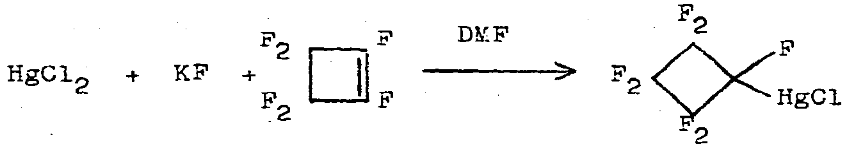
$\boxed{4}$

Full details have been reported concerning the preparation of perfluoroalkylmercurials by the generation of perfluorocarbanions in the presence of mercuric salts (18). The following examples are representative.

$$HgF_2 + 2\,(CF_3)_2C{=}CF_2 \xrightarrow{DMF} Hg\left[C(CF_3)_3\right]_2$$

$$PhHgF + (CF_3)_2C{=}CF_2 \xrightarrow{Et_2O} PhHgC(CF_3)_3$$

$$HgCl_2 + 2\ KF + 2\,CF_3CF{=}CF_2 \xrightarrow{DMF} \left[(CF_3)_2CF\right]_2Hg$$



As reported in Annual Surveys last year (OCR-B, 8 (1971) 428), transfer of secondary alkyl groups from boron to mercury does not occur under mild conditions. This reaction has been studied in greater detail by Larock and Brown (19). The relative reactivities of some tri-sec-alkylboranes in THF toward mercuric benzoate were: cyclopentyl > cyclohexyl > cyclooctyl > sec-butyl > norbornyl. Those reactions with tricyclopentyl- and tricyclohexylborane were of preparative utility, but with only two of the three alkyl groups being cleaved. Boranes containing more bulky alkyl groups reacted extremely slowly with mercuric carboxylates. The reaction with tri-exo-norbornylborane was found to proceed with retention of configuration.

The electrochemical reduction of diphenylthallium bromide in DMF at the dropping mercury electrode resulted in formation of diphenylmercury (20). Phenylmercuric chloride was produced when triphenyltin chloride was treated with mercuric oxide in boiling benzene (21):

$$Ph_3SnCl + HgO \longrightarrow [Ph_3SnOHgCl] \longrightarrow PhHgCl + (Ph_2SnO)_x$$

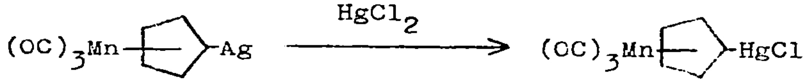
Similarly, the reactions of mercuric halides with bis(triphenyltin) oxide gave phenylmercuric halides, triphenyltin halide and polymeric diphenyltin oxide. Mercuric chloride cleaves vinylic groups from tellurium (22):

$$(Ph_2C{=}CH)_2TeCl_2 \xrightarrow{Hg(OAc)_2} Ph_2C{=}CH\text{-}HgCl$$

Another example of the use of iodonium salts in organomercury synthesis has been published (23):

$$[\mathrm{PhICH{=}CHPh}]\,\mathrm{I} + \mathrm{Hg} \xrightarrow{\text{i-PrOH}} \xrightarrow{\mathrm{SnCl_2}} \mathrm{Ph_2Hg} + (\mathrm{PhCH{=}CH})_2\mathrm{Hg}$$

Organosilver and -gold compounds transfer substituents to mercury, but such reactions are not of preparative utility. Two recent examples are:



(ref. 24)

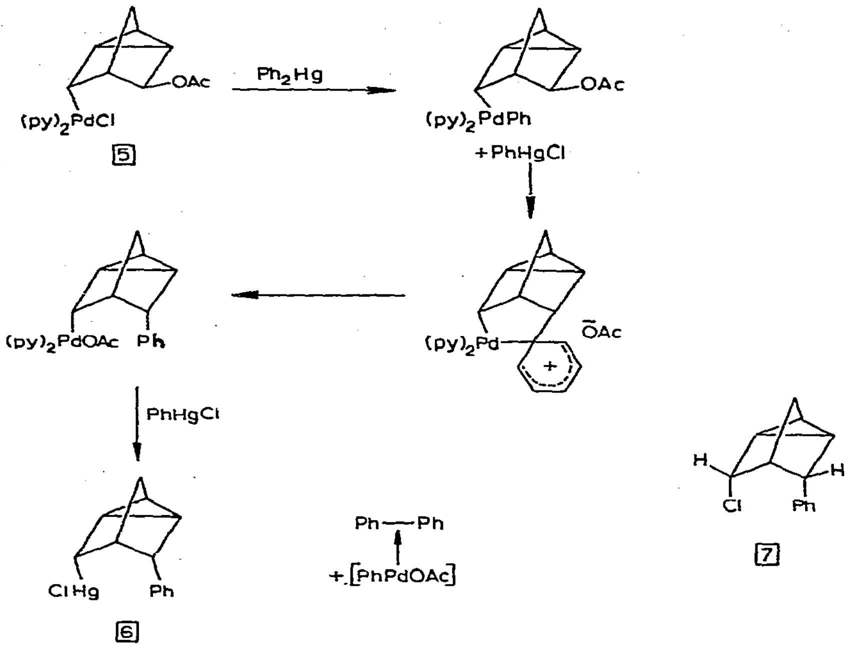
$$\mathrm{PhAu{\cdot}PPh_3} \xrightarrow{\mathrm{HgCl_2}} \mathrm{PhHgCl} + \mathrm{ClAu{\cdot}PPh_3} \qquad \text{(ref. 25)}$$

Of no application in preparative chemistry, but of great importance (in a negative sense) in the biological aspects of organomercury chemistry is the fact that alkyl transfer from primary alkyl cobaloximes and vitamin B_{12} derivatives to mercury(II) salts is a facile process (26-29). It is by such a route that methylmercury compounds are formed in the environment.

Chromium(I) tetraphenylborate reacted with mercuric chloride and phenylmercuric chloride to transfer phenyl groups from boron to mercury (30). Similar phenyl cleavage by mercuric chloride was observed with $(C_6H_6)_2Cr\,[BPh_4]$ (31).

The cleavage of the Fe-C σ bond of π-$C_5H_5Fe(CO)_2CHDCHD$-CMe_3 (<u>threo</u> isomer) by mercuric chloride occurred with retention of configuration at carbon (32).

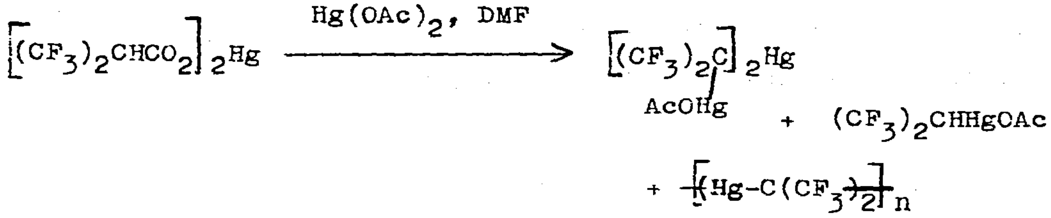
Novel tricyclic mercurials were formed in the reaction of diphenylmercury and diisobutenylmercury with the palladium complex $\boxed{5}$. The mechanism shown below was indicated.



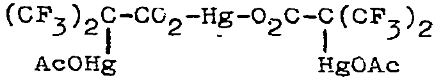
Chlorination of $\boxed{6}$ gave $\boxed{7}$ (33).

The metal displacement reaction involving the interaction of metallic mercury with organic derivatives of other metals has been used preparatively for some time. A study of its mechanism in which a labelled mercury (^{203}Hg) surface was allowed to react with Ph_2TlBr, Ph_2Cd, $Ph_2Mg{\cdot}OEt_2$, Ph_2Zn, Ph_3Bi, Ph_4Sn and Ph_4Pb in benzene medium has been reported (34). It was found that when the Ph_nM structure is approximately linear or planar, the metal displacement reaction occurs. An S_Ei transition state similar to that which obtains in the $Ph_2Hg\text{-}^{*}Hg$ exchange reaction was postulated.

An interesting example of organomercurial synthesis via aliphatic C-H bond mercuration and decarboxylation has been described (35):



$\boxed{8}$ was believed to be the intermediate in this reaction, i.e.



$$\underset{\text{AcOHg}}{(CF_3)_2C}-CO_2-Hg-O_2C-\underset{\text{HgOAc}}{C}(CF_3)_2$$ 8

the sequence of events was mercuration followed by decarboxylation in the formation of the first product.

More examples of the radical-initiated (photochemical or peroxide-catalyzed) decarboxylation of mercuric salts of aliphatic carboxylic acids have been reported by Ol'dekop, Maier and their coworkers.

(ref. 36)

(ref. 37)

(ref. 36)

(ref. 38)

(ref. 38)

Some alkyl mercurials, RHgX (R = n-C_6H_{13}, n-C_7H_{15}, n-C_8H_{17} and cyclo-C_6H_{11}), were prepared by this procedure from mercuric carboxylates which had been generated in situ by oxidation of metallic mercury with 60% hydrogen peroxide and a catalytic amount of nitric acid in the presence of the appropriate carboxylic acid (39).

The role of the solvent in such radical-initiated decarboxylations was investigated (40). Various $(RCO_2)_2Hg$ (R = n-Pr, n-C_6H_{13}, Me, Ph) were decarboxylated in the presence of acyl peroxides, $(R'CO)_2O_2$ (R' = Ph, n-Pr, n-C_6H_{13}). Two products resulted: $RHgO_2CR$ and $R'HgO_2CR$. The former predominated when benzene or n-$PrCO_2H$ were used as solvents, while the latter predominated in reactions carried out in n-heptane or ethyl acetate. A radical chain mechanism was suggested to occur in benzene and n-$PrCO_2H$, a molecular mechanism in heptane and ethyl acetate.

Preparation of organomercurials by elimination of sulfur dioxide rather than carbon dioxide from mercuric salts also has been described (41):

$$Hg(O_2SAr)_2 \longrightarrow Ar_2Hg + 2\ SO_2$$

(Ar = Ph, p-MeC_6H_4, p-BrC_6H_4, p-ClC_6H_4, p-FC_6H_4, 2,3,4-$Cl_3C_6H_2$, 2,4,5-$Cl_3C_6H_2$, 2-naphthyl, 8-quinolyl)

In some cases such SO_2 extrusion occurred at room temperature:

$$2\ \ 2,4,6\text{-}R_3C_6H_2SO_2Na + Hg(OAc)_2 \xrightarrow{H_2O}$$

$$2,4,6\text{-}R_3C_6H_2\text{-}HgO_2SC_6H_2R_3\text{-}2,4,6$$

(for R = Me)

or

$$(2,4,6\text{-}R_3C_6H_2)_2Hg$$

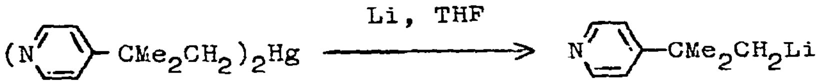
(for R = i-Pr)

3. USE OF ORGANOMERCURIALS IN SYNTHESIS

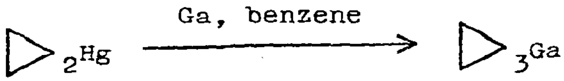
A. ORGANOMETALLIC SYNTHESIS

The metal displacement reaction continues to be useful in the synthesis of organometallic derivatives of other metals from organomercurials. The following examples were published in 1971.

$$(CD_3)_2Hg \xrightarrow{Li,\ Et_2O} CD_3Li$$ (ref. 42)

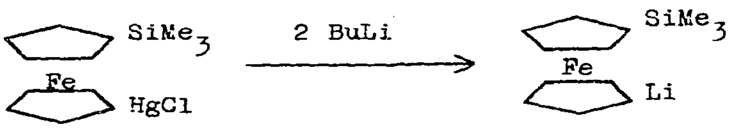

(ref. 43)

$$(PhCH_2)_2Hg \xrightarrow{Al,\ PhMe,\ reflux} (PhCH_2)_3Al$$ (ref. 44)


(ref. 45)

$$(C_6F_5)_2Hg \xrightarrow{In} (C_6F_5)_3In$$ (ref. 46)

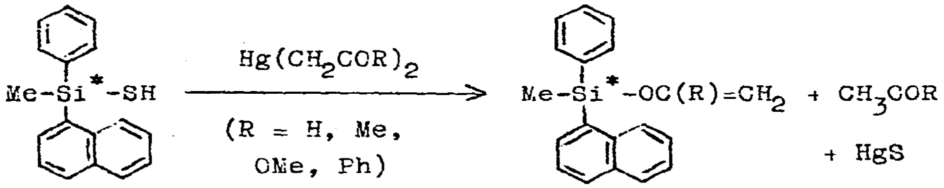
The transmetalation reaction also has found application (47):



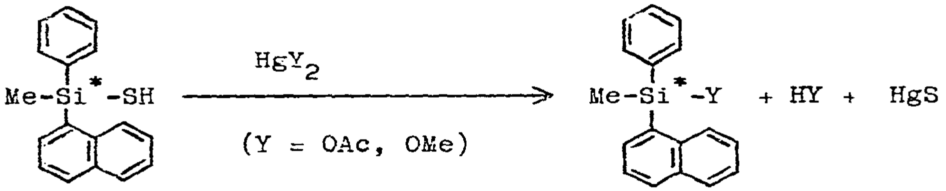
When $(CF_3)_2Hg$ and $(CH_3)_2Cd$ were mixed in pyridine or diglyme solution, alkyl exchange reactions took place, and all possible species were observed: CH_3CdCF_3, $(CF_3)_2Cd$, CH_3HgCF_3, $(CH_3)_2Hg$ and starting compounds (48). Since such exchange reactions are equilibrium processes, the favored formation of CH_3CdCF_3 or $(CF_3)_2Cd$ is determined by the relative concentrations of the starting materials. Although this system only was studied by nmr spectroscopy, preparative applications should be possible.

Alkylation of various derivatives of other metals and metalloids by organomercurials may be noted.

$$Me_2Hg + B_2Cl_4 \longrightarrow MeClBBCl_2 + MeHgCl \qquad \text{(ref. 49)}$$



Ref. 50



(It was found that these substitution reactions at silicon proceeded with inversion of configuration. Similar displacement reactions were observed with $MePh(\alpha\text{-Np})Si^*\text{-}SSiMe_3$.)

$$Ph_2PH + Hg(CH_2CHO)_2 \xrightarrow{DME} Ph_2POCH{=}CH_2 \qquad \text{(ref. 51)}$$

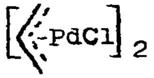
$$Ph_2PK + ClHgCH_2COMe \xrightarrow{DME} Ph_2POCMe{=}CH_2 \qquad \text{(ref. 51)}$$

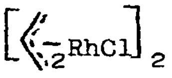
$$\underset{(R\,=\,Me,\ Et,\ Pr,\ Bu)}{Ph_2PH + Hg(CH_2COR)_2} \xrightarrow{benzene} Ph_2PCH_2COR \qquad \text{(ref. 51)}$$

$$RSeSeR + R'_2Hg \xrightarrow{dioxane} 2\ RSeR' + Hg \qquad \text{(ref. 52)}$$

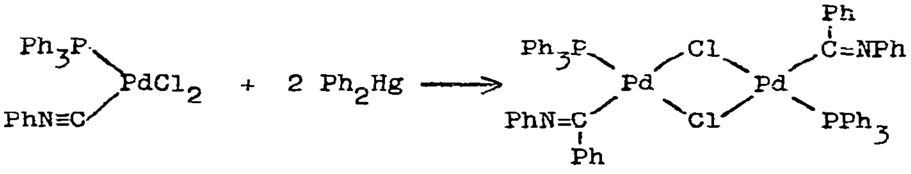
$$RTeTeR + R'_2Hg \xrightarrow{\text{dioxane}} 2\ RTeR' + Hg$$ (ref. 52)

$$PhICl_2 + PhCH{=}CHHgBr \longrightarrow \underset{\text{(low yield)}}{[PhCH{=}CHIPh]I}$$ (ref. 23)

Na_2PdCl_4 + 2 $CH_2{=}CHCH_2HgCl$ $\longrightarrow$  + 4 NaCl + 2 $HgCl_2$ (ref. 53)

2 Na_3RhCl_6 + 4 $CH_2{=}CHCH_2HgCl$ $\longrightarrow$  + 6 NaCl + 4 $HgCl_2$ (ref. 53)

In other examples, organomercury compounds have reacted with σ-bonded ligands in transition metal complexes to give transformed ligand systems.



+ 2 PhHgCl (ref. 54)

$$HCCo_3(CO)_9 + \underset{(X = I\ \text{or}\ Br)}{(XCH_2)_2Hg} \longrightarrow CH_3CCo_3(CO)_9$$ (ref. 55)

The latter reaction most likely does not proceed via CH_2 insertion into the exocluster C-H bond, but rather by way of an alkylation-reduction or a reduction-alkylation sequence (55).

(Note the arylation and alkylation of methylidynetricobalt nonacarbonyl complexes with organomercurials: OCR-B, 8 (1971) 439).

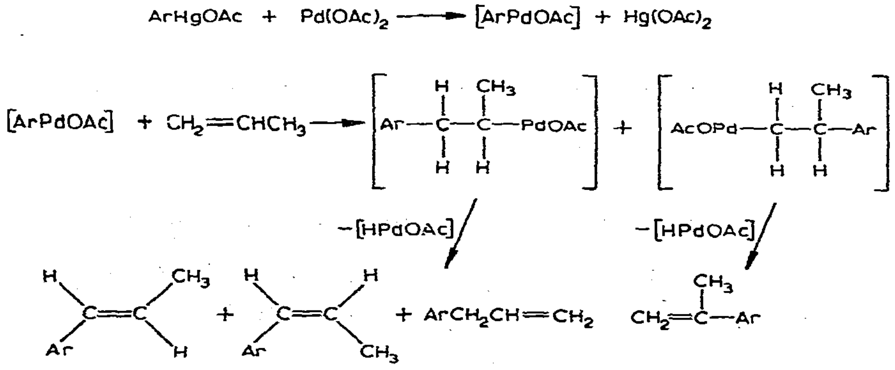
B. ORGANIC SYNTHESIS

Organic syntheses in which organomercurials are used to generate an organic derivative of another metal (often in situ) which then is oxidized or otherwise treated to give an organic product are becoming more numerous. (Note previous examples in OCR-B, 8 (1971) 441 and OCR-B, 6 (1970) 246, 248).

A new, high yield synthesis of phenols involves the arylation of diborane with organomercuric halides and oxidation of the arylboranes thus formed (without their prior isolation) (56):

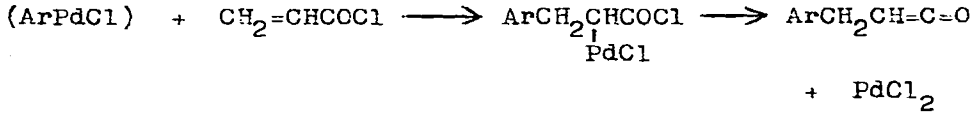
$$\mathrm{ArHgX} \xrightarrow{B_2H_6,\ \mathrm{THF}} \mathrm{ArB}\langle \xrightarrow{H_2O_2,\ \mathrm{NaOH}} \mathrm{ArOH}$$

The generation of reactive organopalladium intermediates from organomercurials has found further application in organic synthesis. Heck has reported further examples of the arylation and carboalkoxylation of olefins using organomercury/$Pd(OAc)_2$ systems (57). The products formed can be explained in terms of the following sequence:



Tables I - IV present the results reported. It would appear that the addition is sterically controlled for the most part. A catalytic (in $PdCl_2$) synthesis of ketene derivatives was developed, but product yields were low (58):

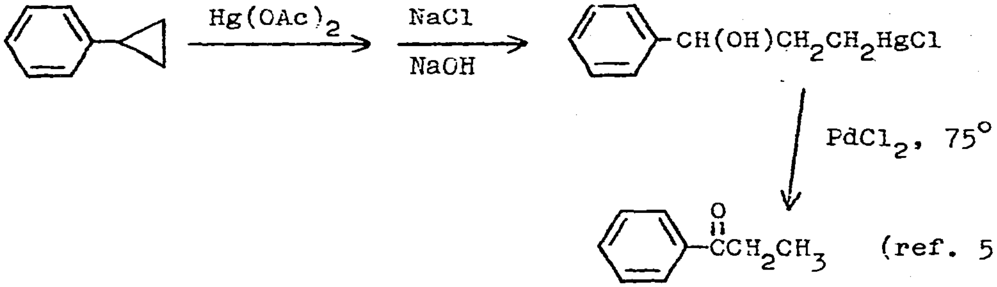
$$ArHgCl + PdCl_2 \longrightarrow (ArPdCl) + HgCl_2$$



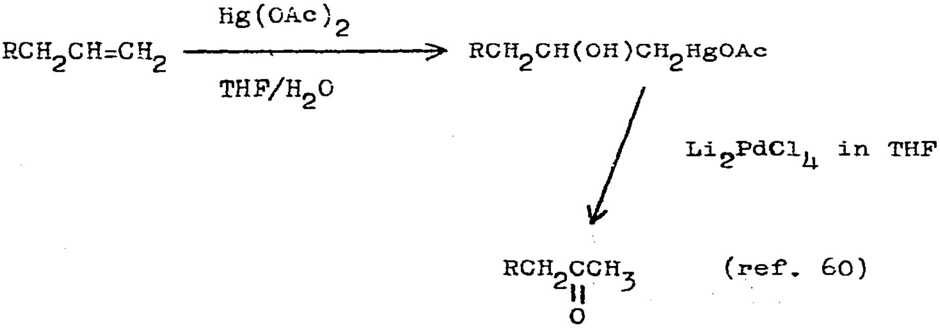
$$(ArPdCl) + CH_2{=}CHCOCl \longrightarrow ArCH_2\underset{\substack{|\\PdCl}}{C}HCOCl \longrightarrow ArCH_2CH{=}C{=}O + PdCl_2$$

The ketene was isolated as its alcoholysis product, $ArCH_2CH_2$-CO_2R.

The oxymercuration reaction followed by organic group transfer to palladium and oxidation of the organopalladium intermediate has served in the synthesis of ketones:



(ref. 59)



(ref. 60)

In the latter reaction, excellent ketone yields were obtained

TABLE I

REACTIONS OF VARIOUS "ARYLPALLADIUM SALTS" WITH PROPYLENE[a] (ref. 57)

Mercurial used to prepare arylpalladium salt	Solvent	Products					Internal addition/terminal addition
		Total yield, %	% *trans*-1-aryl-1-propene	% *cis*-1-aryl-1-propene	% 1-aryl-2-propene	% 2-aryl 2-propene	
p-$CH_3OC_6H_4HgOAc$[b]	CH_3CN	74	50	3	4	43	1.3
p-$CH_3OC_6H_4HgCl$[b]	CH_3CN	7	54	10	~0	36	1.8
C_6H_5HgOAc[b]	CH_3CN	102	57	5	12	26	2.8
C_6H_5HgOAc[b]	CH_3OH	66	60	9	15	16	5.3
C_6H_5HgOAc[b]	CH_3COOH	87	63	7	14	16	5.3
C_6H_5HgOAc	THF	102	51	6	27	16	5.3
C_6H_5HgOAc	C_6H_6	95	48	7	29	16	5.3
C_6H_5HgOAc	CH_2Cl_2	122[c]	56	8	20	16	5.3
C_6H_5HgOAc	Monoglyme	96	52	7	24	17	4.9
C_6H_5HgOAc	Diglyme	71	54	7	22	17	4.9
p-$CH_3OCOC_6H_4HgOAc$	CH_3CN	95	58		18	24	3.2
p-$CH_3OCOC_6H_4HgCl$	CH_3CN	99	82			18	4.6

[a] Carried out at 30° with 30 psig of propylene for 1 hr. Mercurial and palladium salts always had the same anion in each reaction.

TABLE II

REACTIONS OF PHENYLPALLADIUM ACETATE WITH VARIOUS OLEFINIC COMPOUNDS[a] (ref. 57)

Olefinic compound	Products, % yields	
	Terminal substitution	Internal substitution
$CH_2{=}CHCOOCH_3$	*trans*-$C_6H_5CH{=}CHCOOCH_3$, 84	~0
$CH_2{=}CHCHO$	*trans*-$C_6H_5CH{=}CHCHO$, 85	~0
$CH_2{=}CHCN$	*trans*-$C_6H_5CH{=}CHCN$, 26; *cis*-$C_6H_5CH{=}CHCN$, 17	~0
$CH_2{=}CHCH_2Cl$[b]	$C_6H_5CH_2CH{=}CH_2$, 37; *trans*-$C_6H_5CH{=}CHCH_3$, 11	~0
$CH_2{=}CHOAc$[c]	*trans*-$C_6H_5CH{=}CHOAc$, 31; *cis*-$C_6H_5CH{=}CHOAc$, 14	$C_6H_5CH{=}CH_2$, 0.2; *trans*-$C_6H_5CH{=}CHC_6H_5$, 4[d]
$CH_2{=}CHC_6H_5$	*trans*-$C_6H_5CH{=}CHC_6H_5$, 78; *cis*-$C_6H_5CH{=}CHC_6H_5$, <1	$CH_2{=}C(C_6H_5)_2$, <1
$CH_2{=}CHCH_3$[e]	*trans*-$C_6H_5CH{=}CHCH_3$, 57; *cis*-$C_6H_5CH{=}CHCH_3$, 5; $C_6H_5CH_2CH{=}CH_2$, 12	$CH_2{=}C(C_6H_5)CH_3$, 26
$CH_2{=}CH(CH_2)_3CH_3$	$C_6H_5CH{=}CH(CH_2)_3CH_3$, 47; $C_6H_5CH_2CH{=}CH(CH_2)_2CH_3$, 7	$CH_2{=}C(C_6H_5)(CH_2)_3CH_3$, 18
trans-$C_2H_5CH{=}CHC_2H_5$	$C_2H_5CH(C_6H_5)CH{=}CHCH_3$, 48; $C_2H_5C(C_6H_5){=}CHCH_2CH_3$, 30	
$CH_2{=}CHCH_2OH$	$C_6H_5CH_2CH_2CHO$, 35; $C_6H_5CH{=}CHCHO$, 13[f]	$CH_2{=}C(C_6H_5)CHOH$, 5; $CH_3CH(C_6H_5)CHO$, 4
$CH_2{=}CHCH_2COOCH_3$	$C_6H_5CH{=}CHCH_2COOCH_2$, 54; $C_6H_5CH_2CH{=}CHCOOCH_3$ (?), 4	$CH_2{=}C(C_6H_5)CH_2COOCH_3$, 4
$CH_2{=}CHCH_2CN$	$C_6H_5CH{=}CHCH_2CN$, 45; $AcOCH_2CH{=}CHCN$, 55	~0
$CH_2{=}CHCH_2CH_2Cl$[b]	*trans*-$C_6H_5CH{=}CHCH_2CH_2Cl$, 36	~0
$CH_2{=}CHCH_2OAc$	*trans*-$C_6H_5CH{=}CHCH_2OAc$, 89; *cis*-$C_6H_5CH{=}CHCH_2OAc$, 5	$CH_2{=}C(C_6H_5)CH_2OAc$, 5
$CH_2{=}CHCH_2CH(OH)CH_3$	$C_6H_5CH{=}CHCH_2CH(OH)CH_3$, 59	Low
$CH_2{=}CH(CH_2)_3OH$	$C_6H_5CH{=}CH(CH_2)_3OH$, 28	$CH_2{=}C(C_6H_5)(CH_2)_3OH$, 18

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[a] All reactions carried out in acetonitrile solution at room temperature. [b] Treated with "phenylpalladium chloride" rather than the acetate.

TABLE III

PHENYLATION OF VARIOUS METHYL-SUBSTITUTED ALLYL ALCOHOLS[a] (ref. 57)

Allylic alcohol	3-Phenylated products	2-Phenylated products
$CH_2{=}CHCH_2OH$	$C_6H_5CH_2CH_2CHO$, 35; $C_6H_5CH{=}CHCHO$, 13	$CH_2{=}C(C_6H_5)CH_2OH$, 5; $CH_3CH(C_6H_5)CHO$, 4
trans-$CH_3CH{=}CHCH_2OH$	$C_6H_5CH(CH_3)CH_2CHO$, 38	$CH_3CH_2(C_6H_5)CHO$, ~1
trans-$CH_3CH{=}CHC(OH)HCH_3$	$C_6H_5CH(CH_3)CH_2COCH_3$, 44	<5%
$(CH_3)_2C{=}CHC(OH)HCH_3$	$(CH_3)_2C(C_6H_5)CH_2COCH_3$, 29	<5%

[a] All reactions were carried out in acetonitrile solution with phenylmercuric acetate and a stoichiometric amount of palladium acetate at 0° with completion at room temperature.

when only catalytic amounts of Li_2PdCl_4 were used and copper (II) chloride was added to reoxidize the palladium metal formed. Methanol proved to be the solvent of choice.

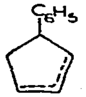
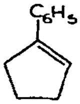
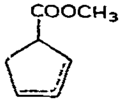
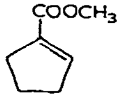
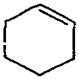
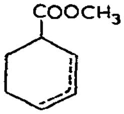
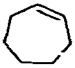
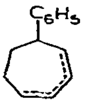
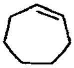
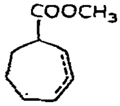
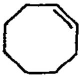
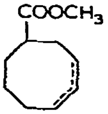
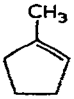
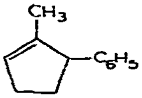
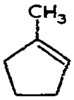
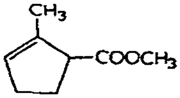
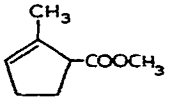
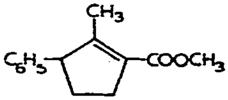
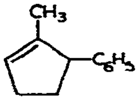
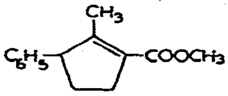
Another new ketone synthesis is based on the stoichiometric reaction of organomercuric halides with nickel tetracarbonyl (61):

$$2\ ArHgX + Ni(CO)_4 \xrightarrow{DMF,\ 60-70^{\circ}} \underset{(>90\%)}{Ar_2C{=}O} + 2\ Hg + 3\ CO + NiX_2$$

Other solvents (MeCN, DMSO) may be used. Dialkyl ketones could be prepared by this procedure using alkylmercuric halides, but product yields were lower (55-65%). The reaction course

TABLE IV

PHENYLATION AND CARBOMETHOXYLATION OF CYCLIC OLEFINS[a] (ref. 57)

Cyclic olefin	Mercurial	Product	Isomeric composition by glc	% yield
	C_6H_5HgOAc		47 29	76
				5
	$CH_3OCOHgOAc$		53 25	78
				0.5
	$CH_3OCOHgOAc$		8 7	15
	C_6H_5HgOAc		29 21 10	60
	$CH_3OCOHgOAc$		48 15	63
	$CH_3OCOHgOAc$		24 29	53
	C_6H_5HgOAc			83
	$CH_3OCOHgOAc$			76
	C_6H_5HgOAc			62
	$CH_3OCOHgOAc$			20

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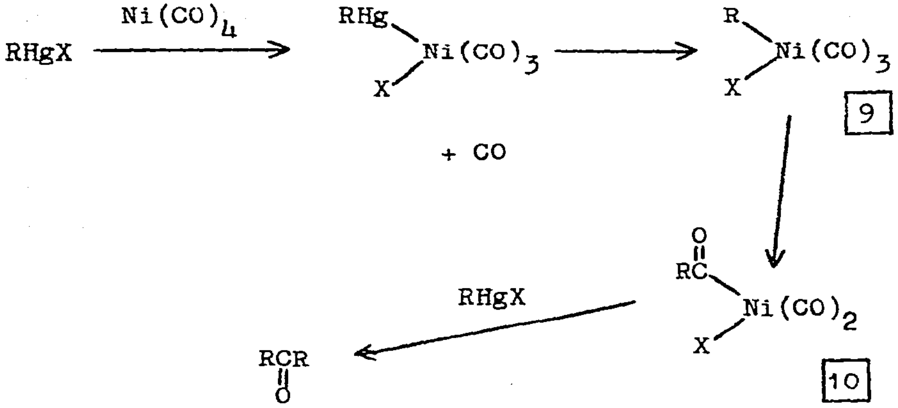
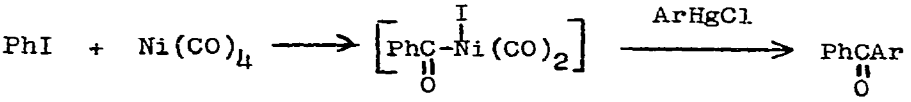
[a] All reactions were carried out in acetonitrile solution with stoichiometric amounts of palladium acetate. Reactions were begun at 0° and after 30 min continued at room temperature for 15 hr.

shown below was suggested:



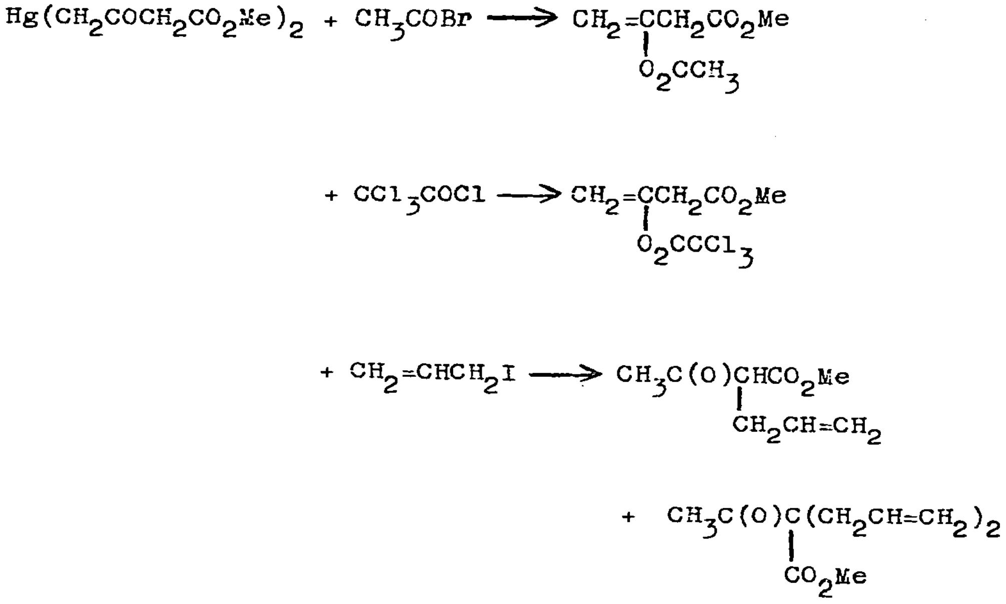
With phenylmercuric acetate, diphenylmercury rather than benzophenone was formed, presumably by reaction of intermediates $\boxed{9}$ and $\boxed{10}$ (X = OAc) with PhHgOAc. Of special interest is the reaction of nickel tetracarbonyl and iodobenzene in the presence of p-tolylmercuric chloride, which gave $C_6H_5COC_6H_4Me$-p (68%), $(p\text{-}MeC_6H_4)_2CO$ (30%) and $(C_6H_5)_2CO$ (3%). The first product was the result of the reaction shown below.



$$PhI + Ni(CO)_4 \longrightarrow \left[PhC(=O)\text{-}Ni(I)(CO)_2\right] \xrightarrow{ArHgCl} PhC(=O)Ar$$

Presumably the reaction of iodobenzene with nickel tetracarbonyl competes quite effectively with the ArHgCl + $Ni(CO)_4$ reaction. The drawback of this new synthetic chemistry is that the extremely toxic and volatile nickel tetracarbonyl is required as a stoichiometric reagent and for this reason the prospects for its general application in synthesis are poor.

Reactions of γ-mercurated acetoacetic esters with reactive organic halides have been described (62):



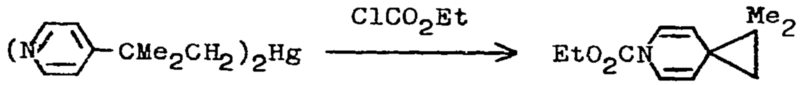
$$Hg(CH_2COCH_2CO_2Me)_2 + CH_3COBr \longrightarrow CH_2{=}\underset{\substack{|\\ O_2CCH_3}}{C}CH_2CO_2Me$$

$$+ CCl_3COCl \longrightarrow CH_2{=}\underset{\substack{|\\ O_2CCCl_3}}{C}CH_2CO_2Me$$

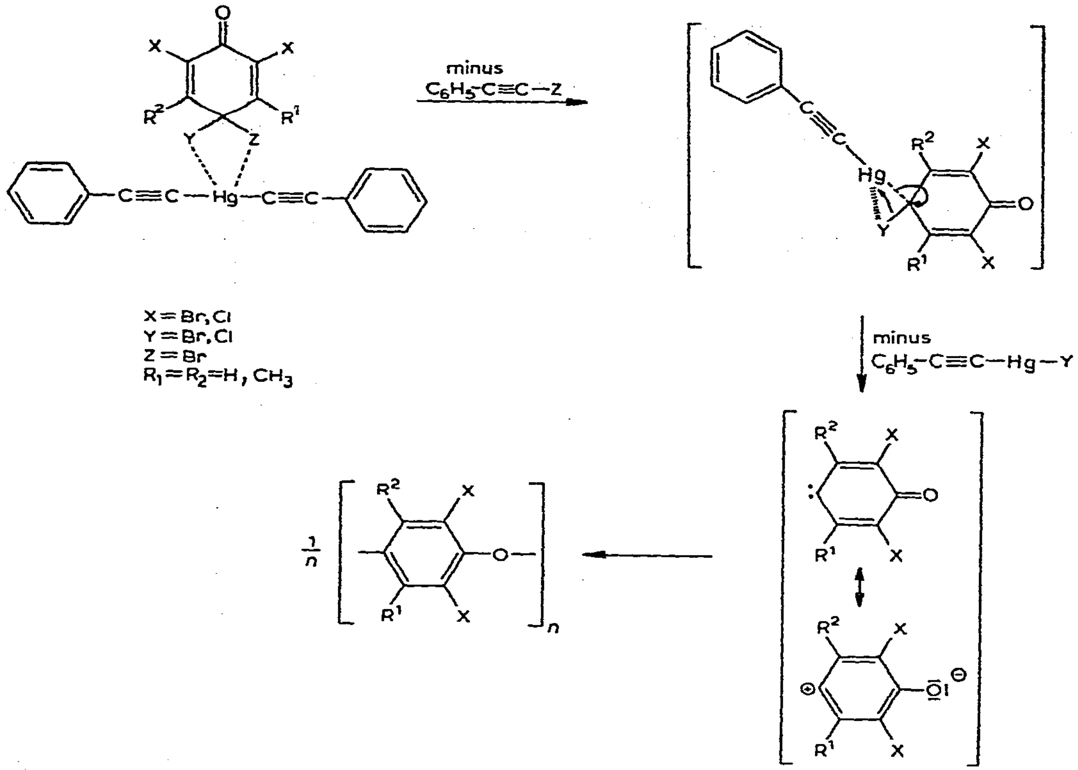
$$+ CH_2{=}CHCH_2I \longrightarrow CH_3C(O)\underset{\substack{|\\ CH_2CH{=}CH_2}}{C}HCO_2Me$$

$$+ CH_3C(O)\underset{\substack{|\\ CO_2Me}}{C}(CH_2CH{=}CH_2)_2$$

Another reaction of interest is (43):



The mechanism of the preparatively useful reaction of bis(phenylethynyl)mercury with 4,4-dihalo-2,5-cyclohexadienones has been studied (63) (cf. OCR-B, 6 (1970) 248). In general, poly(p-phenylene oxides) were produced in these reactions (Table V). 2,3,4,4,5,6-Hexabromo-2,5-cyclohexadienone reacted differently:


minus
C6H5-C≡C-Z
minus
C6H5-C≡C-Hg-Y
X = Br, Cl
Y = Br, Cl
Z = Br
R1 = R2 = H, CH3

but:

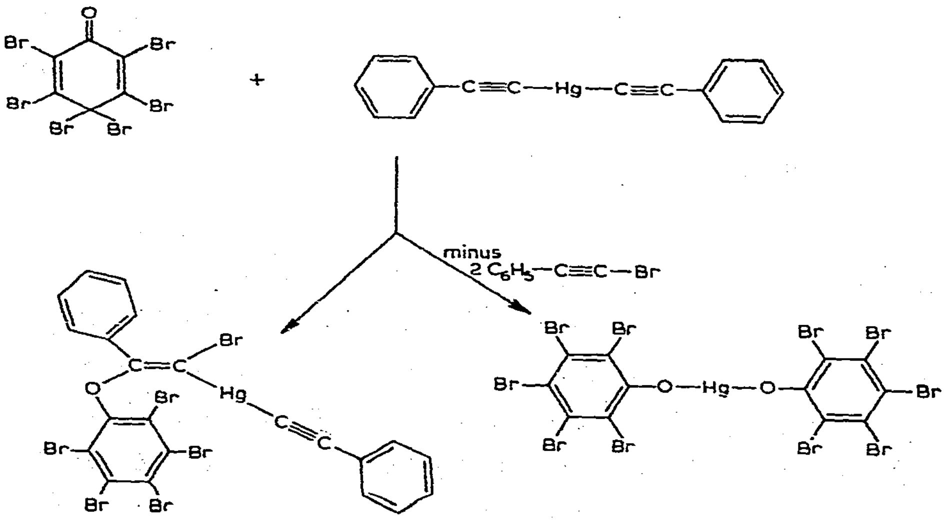
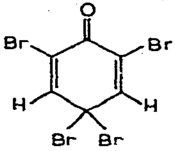
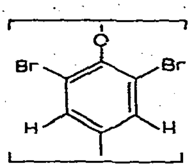
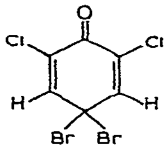
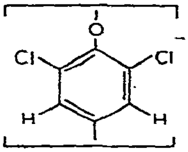
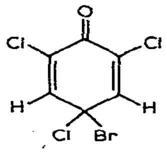
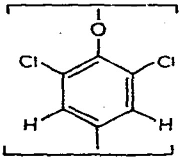
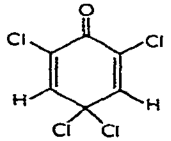
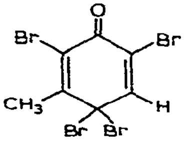
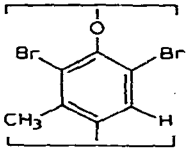
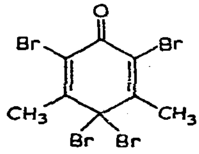
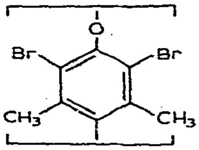
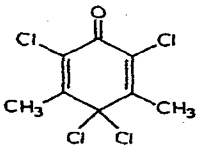
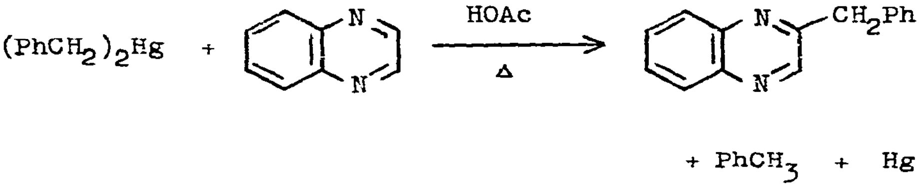

minus
2 C6H5-C≡C-Br

TABLE V

REACTIONS OF $(PhC{\equiv}C)_2Hg$ WITH SUBSTITUTED 4,4-DIHALO-2,5-CYCLOHEXADIENONES IN THF

Starting compound	Average mol. wt.	Average dec. p.	Yield (%)	Polymer formed
	~13000 ± 650	~50	~90	
	~9700 ± 490	~60	~90	
	~2700 ± 130	~17	10-20	
		no reaction		
	~4630 ± 230	~17	~70	
	~2046 ± 100	~7	~80	
		no reaction		

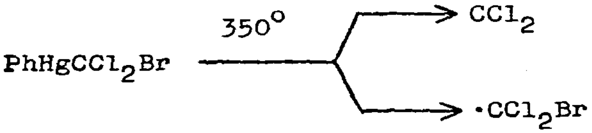
The photolysis or thermolysis of organomercury compounds is a useful method for generating free radicals, and in 1971 the phenylation of anthracene via diphenylmercury photolysis (64) and the benzylation reaction shown below (65) were reported. The photolysis of bis(2-cyanoethyl)mercury in methanol solution resulted in radical dimerization, giving adiponitrile in 90% yield (66).

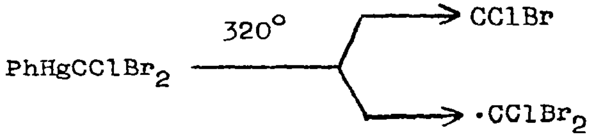


C. HALOMETHYL-MERCURY COMPOUNDS

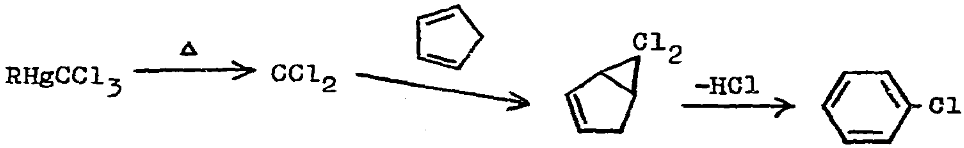
Halomethylmercurials are discussed in this section in view of their excellent utility as divalent carbon transfer agents. Discussion of their reactions and applications can be found in Kirmse's second edition of "Carbene Chemistry" (67).

The thermal decomposition of phenyl(trihalomethyl)mercury compounds in solution at about 80° to give phenylmercuric halide and dihalocarbene has been studied in some detail and has found much application in synthesis (cf. previous volumes of OCR-B and "Annual Surveys of Organometallic Chemistry" for references). Of great interest in this area have been studies of the gas phase pyrolysis of trihalomethyl-mercury compounds by Nefedov and his coworkers and Margrave and Hauge (68-70). Thus, phenyl(trichloromethyl)mercury was decomposed in a high vacuum pyrolysis unit (at 220-390°) which was joined to a liquid helium cryostat. The volatile decomposition products and the argon carrier gas used were condensed on the KBr window of the cryostat. Ir spectroscopic investigation of the species present in the argon matrix showed them to be dichlorocarbene, the trichloromethyl radical, their dimers, C_2Cl_4 and C_2Cl_6, and phenylmercuric chloride. The compounds $Hg(CCl_3)_2$ and CCl_3HgCl were studied in similar manner. Gas phase pyrolysis of $PhHgCCl_2Br$ and $PhHgCClBr_2$ also was studied using the rare gas matrix isolation procedure (71):





It was found that $PhHgCCl_2Br$ is a much more effective source of dichlorocarbene than is $PhHgCCl_3$, in agreement with previous solution studies (Seyferth et al., 1965). While the decomposition of these mercurials at lower temperatures in solution will continue to find major application in dihalocarbene generation for preparative purposes, such gas phase reactions can be used in synthesis. Thus, the gas phase pyrolysis of $PhHgCCl_3$ or $Hg(CCl_3)_2$ in the presence of cyclopentadiene gave chlorobenzene by the route shown below (68):

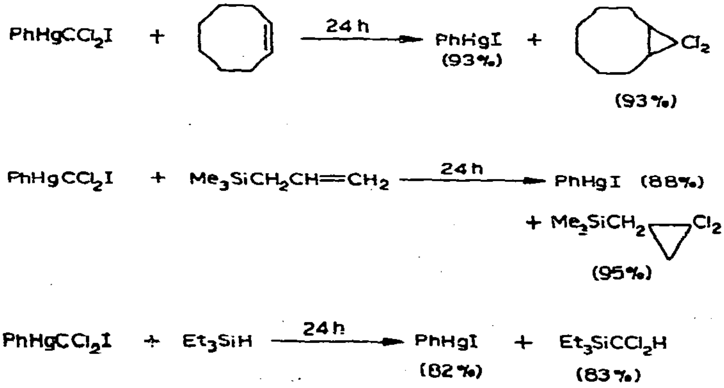


In connection with this work, Nefedov et al. (72) carried out detailed infrared and mass spectroscopic studies of phenyl(trichloromethyl)mercury and diphenylmercury.

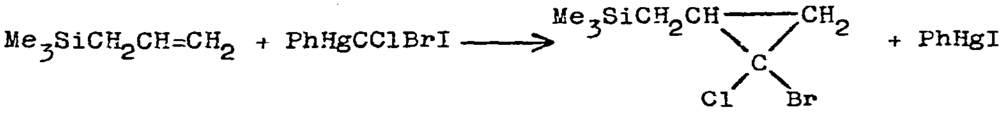
The preparation of phenyl(trihalomethyl)mercury compounds which release a dihalocarbene in solution at room temperature at a fairly rapid rate represents a notable advance in the halomethyl-mercury/carbene area. The most reactive of this new generation of halomethylmercurials is $PhHgCCl_2I$, prepared as follows (73):

$$PhHgCl + HCCl_2I + Me_3COK \xrightarrow{THF/Et_2O,\ -55^{\circ}} PhHgCCl_2I + KCl + Me_3COH$$

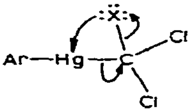
At 80° in benzene solution, this reagent reacts with cyclohexene almost instantaneously to give 7,7-dichloronorcarane in 85% yield. A similar reaction carried out at room temperature was complete within 24 hr. and gave 7,7-dichloronorcarane in 89% yield. This mercurial even transferred CCl_2 to cyclohexene (in 71% yield) at 0°., but a reaction time of 8 days was required. Other room temperature reactions of this new organomercury reagent are shown below.



Phenyl(iodobromochloromethyl)mercury was less reactive (74). At 80° in benzene solution, it transferred CClBr to cyclooctene, allyltrimethylsilane and triethylsilane during a reaction time of 3-4 min.; at room temperature, such transfer reactions required 4 days to achieve high yields of product.



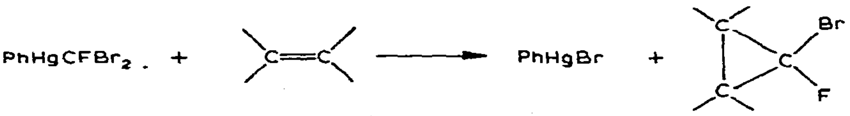
The high reactivity of $PhHgCCl_2I$ and PhHgCClBrI, in comparison with that of $PhHgCCl_2Br$ and $PhHgCClBr_2$, can be understood in terms of the transition state $\boxed{11}$, previously suggested for



$\boxed{11}$

such dihalocarbene extrusion from phenyl(trihalomethyl)mercury compounds. One might expect nucleophilic attack at mercury by iodine to be more favorable and, furthermore, the C-I bond is weaker than the C-Br bond.

Phenyl(dibromofluoromethyl)mercury also was found to be a very reactive divalent carbon transfer agent, and it provides a good route to bromofluorocarbene (74).

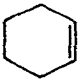
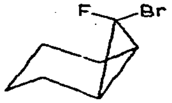
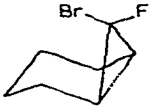
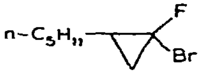
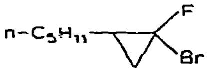
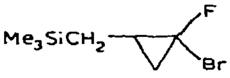
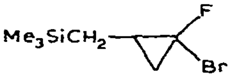


Its reactions at 80° and at room temperature are summarized in Table VI.

The substitution of the phenyl group in $PhHgCCl_3$ and

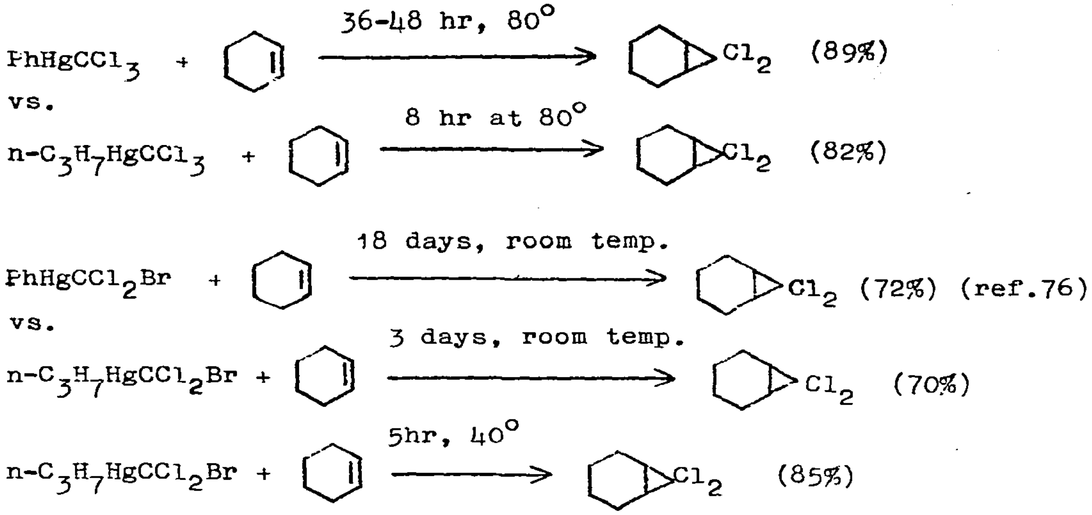
TABLE VI (ref. 74)

REACTIONS OF PHENYL(DIBROMOFLUOROMETHYL)MERCURY[a]

Substrate	Reaction temp. (°C/time)	Product[b]	Yield (%)
	25°/ 3 days	 (I)	32
		 (II)	58
	80°/20 min.	I II	30 58
n-$C_5H_{11}CH=CH_2$	25°/ 3 days	 (mixed isomers)	78
n-$C_5H_{11}CH=CH_2$	80°/20 min.	 (mixed isomers)	72
$Me_3SiCH_2CH=CH_2$	25°/ 3 days	 (mixed isomers)	60
$Me_3SiCH_2CH=CH_2$	80°/20 min.	 (mixed isomers)	70
Et_3SiH	25°/ 3 days	$Et_3SiCHFBr$	55
Et_3SiH	80°/20 min.	$Et_3SiCHFBr$	92

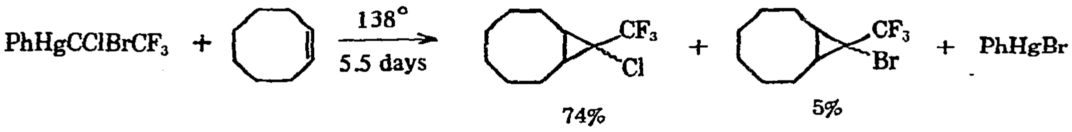
[a] 30 mmol of substrate, 4–5 mmol of $PhHgCFBr_2$ in 10 ml of dry benzene, with stirring under nitrogen. [b] Phenylmercuric bromide was obtained in high yield in each reaction.

PhHgCCl$_2$Br by n-propyl groups was found by Shcherbakov (75) to lead to more reactive CCl$_2$ transfer agents.



n-Propyl(trichloromethyl)mercury also was used to insert CCl$_2$ into the benzylic C-H bond of cumene (36%), into the SiH bond of triethylsilane (48%) and into the Sn-Sn bond of hexamethylditin (40%), in reactions carried out for 5 hr. at 80°.

Details have been reported concerning a number of new halomethyl-mercury compounds. The fluorine-containing mercurial PhHgCClBrCF$_3$ was found to transfer CF$_3$CCl to carbenophilic substrates, but relatively high reaction temperatures were required (77):

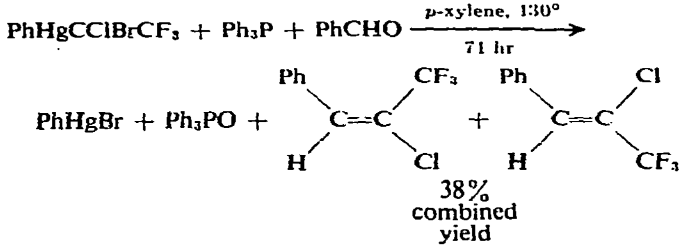


The yields of gem-CF$_3$,Cl-substituted cyclopropanes obtained on reaction of this reagent with other olefins were variable

($Me_2C{=}CMe_2$, 58%; $Me_2C{=}CHMe$, 46%; cyclohexene, 41%; Me_3SiCH_2-$CH{=}CH_2$, 9%; cis-$MeCH{=}CHMe$, 27%), and this very likely reflects the instability of the product cyclopropanes under the reaction conditions. An insertion reaction into the Si-H bond also was reported:

$$PhHgCClBrCF_3 \xrightarrow[130^\circ,\ 6\ days]{Et_3SiH} \underset{(52\%)}{Et_3SiCHClCF_3} + \underset{(3\%)}{Et_3SiCHBrCF_3} + \underset{(83\%)}{PhHgBr}$$

and this mercury reagent also was used to generate a phosphorus ylide:

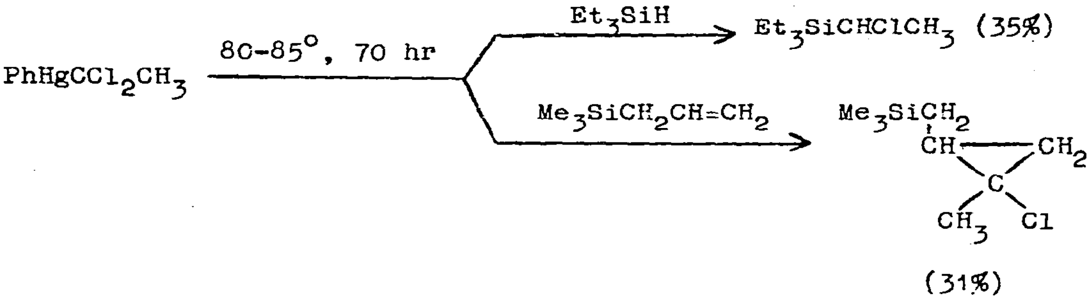


The action of sodium iodide in DME on $PhHgCClBrCF_3$ resulted in displacement of CF_3CClBr^-, but this anion underwent β-elimination of fluoride ion (rather than α-elimination of bromide ion) to give $CF_2{=}CClBr$. The compound $PhHgCCl_2CF_3$, as expected, was much more stable than $PhHgCClBrCF_3$, and its high stability precluded its application in cyclopropane synthesis. These mercurials were prepared from the respective pentahaloethane:

$$PhHgCl + Me_3COK + CF_3CXClH \xrightarrow{THF,\ -10\ to\ 0^\circ} PhHgCXClCF_3 + Me_3COH + KCl \quad (3)$$

X = Cl, 75%
X = Br, 86%

Also prepared was $PhHgCCl_2CH_3$ (via $LiCCl_2CH_3$) (78). This compound was found to transfer CH_3CCl in isolated cases:



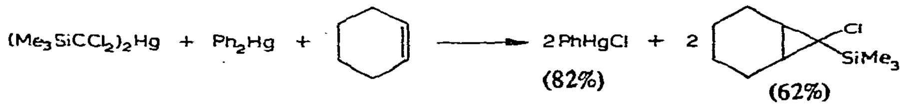
However, the major mode of decomposition of this mercury compound in the presence of less reactive substrates involved elimination of HCl:

$$PhHgCCl_2CH_3 \longrightarrow PhHgCCl{=}CH_2 + HCl$$

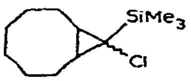
with the formation of secondary products due to C-Hg cleavage by HCl and redistribution reactions. The decomposition of $PhHgCCl_2CH_3$ in chlorobenzene at 80° gave PhHgCl (17%), $CH_2{=}CClHgCl$ (30%), CH_3CCl_2HgCl (16%), C_6H_6 (67%), $(CH_2{=}CCl)_2Hg$ and $CH_3CCl_2HgCCl{=}CH_2$. The equations below summarize the chemistry which possibly is responsible for the formation of these products.

$$PhHgCCl_2CH_3 \rightarrow PhHgCCl{=}CH_2 + HCl$$
$$PhHgCCl_2CH_3 + HCl \rightarrow C_6H_6 + ClHgCCl_2CH_3$$
$$PhHgCCl{=}CH_2 + HCl \rightarrow C_6H_6 + ClHgCCl{=}CH_2$$
$$PhHgCCl_2CH_3 + ClHgCCl{=}CH_2 \rightarrow PhHgCl + CH_3CCl_2HgCCl{=}CH_2$$
$$CH_3CCl_2HgCCl{=}CH_2 \rightarrow Hg(CCl{=}CH_2)_2 + HCl$$
$$ClHgCCl_2CH_3 \rightarrow ClHgCCl{=}CH_2 + HCl$$
$$2\ PhHgCCl_2CH_3 \rightarrow Ph_2Hg + Hg(CCl_2CH_3)_2$$
$$(CH_3CCl_2)_2Hg \rightarrow CH_3CCl_2HgCCl{=}CH_2 + HCl$$

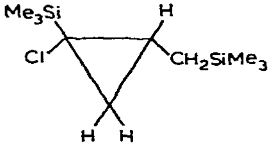
Trimethylsilyl-substituted mercury compounds which serve as sources of silyl-substituted carbenes have been prepared by organolithium or Grignard procedures (OCR-B, 8 (1971) 460). Bis(trimethylsilyldichloromethyl)mercury reacted with cyclohexene in the presence of an equimolar quantity of diphenylmercury (10 days at 118°) to give the expected norcarane derivative (79):



A similar reaction with cyclooctene (125-135°, for 8 days in chlorobenzene) gave $\boxed{12}$ in 73% yield, while reaction with allyltrimethylsilane resulted in the expected $\boxed{13}$. Minor by-products indicative of a free radical side-reaction (Me_3SiCCl_2H, $Me_3SiCCl{=}CCl_2$) were formed in these reactions, and at 220° such free radical chemistry predominated. Thermolysis of $(Me_3SiCCl_2)_2Hg$ at 220° gave Me_3SiCCl_2H, Me_3SiCCl_3, $Me_3SiCCl{=}CCl_2$, Me_3SiCl and $Me_3SiCCl{=}CClSiMe_3$. The latter is best rationalized in terms of a carbene process:

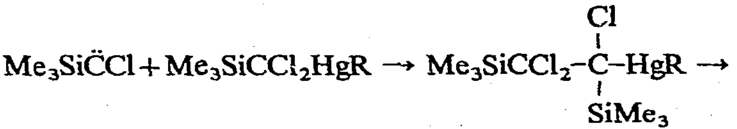


$\boxed{12}$



$\boxed{13}$

$$Me_3SiCCl_2HgCCl_2SiMe_3 \rightarrow Me_3Si\ddot{C}Cl + Me_3SiCCl_2HgCl$$



$$Me_3Si\ddot{C}Cl + Me_3SiCCl_2HgR \rightarrow Me_3SiCCl_2{-}\underset{SiMe_3}{\overset{Cl}{C}}{-}HgR \rightarrow$$

$$\xrightarrow{\beta\text{-elimination}} Me_3SiCCl{=}CClSiMe_3 + RHgCl$$

but the others result from the initially formed $Me_3SiCCl_2\cdot$ radical:

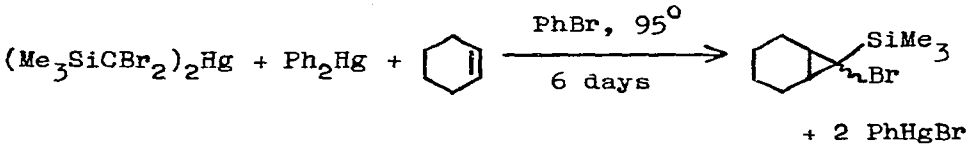
$$(Me_3SiCCl_2)_2Hg \xrightarrow{220°} 2\,Me_3Si\dot{C}Cl_2 + Hg$$

$$Me_3Si\dot{C}Cl_2 \xrightarrow{RH} Me_3SiCCl_2H$$

$$Me_3Si\dot{C}Cl_2 \xrightarrow{RCl} Me_3SiCCl_3$$

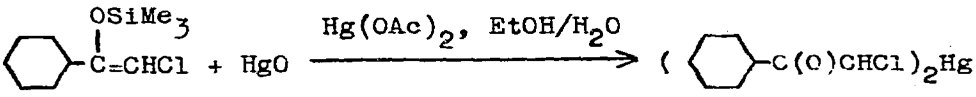
$$2\,Me_3Si\dot{C}Cl_2 \rightarrow [Me_3SiCCl_2CCl_2SiMe_3] \rightarrow$$
$$\rightarrow Me_3SiCCl{=}CCl_2 + Me_3SiCl$$

Bis(trimethylsilyldibromomethyl)mercury is a reasonably good source of Me_3SiCBr (79):



On the other hand, $(Me_3SiCHBr)_2Hg$ was too stable for application as a divalent carbon transfer agent. After it had been heated in the presence of cyclohexene at 160° for 7 days, phenylmercuric bromide had been formed to the extent of only 19% and Me_3SiCH-derived products (7-trimethylsilylnorcarane and 1,2-bis(trimethylsilyl)ethylene) were found in only low yield At higher temperatures (190-210°), homolytic C-Hg fission predominated (79).

Another halomethyl-mercurial which was prepared and which was too stable to show divalent carbon transfer reactivity was $\boxed{14}$ (80).



$\boxed{14}$

New syntheses of known halomethylmercurials have been reported. The reaction sequence shown below makes $PhHgCF_3$ readily available from easily accessible starting materials (81). This mercurial is an excellent source of CF_2 when it is

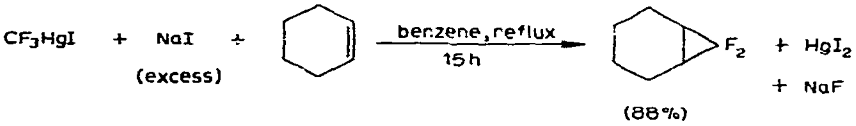
$$2\,CF_3CO_2H + HgO \xrightarrow{\text{watei}} (CF_3CO_2)_2Hg + H_2O$$

$$(CF_3CO_2)_2Hg \xrightarrow{300^\circ} CF_3HgO_2CCF_3 + CO_2$$

$$CF_3HgO_2CCF_3 + NaI \rightarrow CF_3HgI + CF_3CO_2Na$$

$$CF_3HgI + Ph_2Hg \rightarrow PhHgCF_3 + PhHgI$$

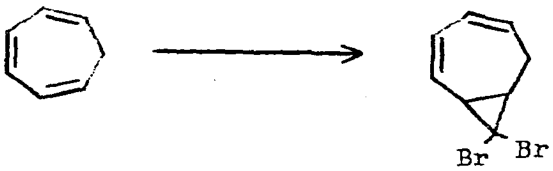
treated with sodium iodide in benzene at 80° (OCR-B, 6 (1970) 250), and the CF_3HgI intermediate in the preparation above also transfers CF_2:



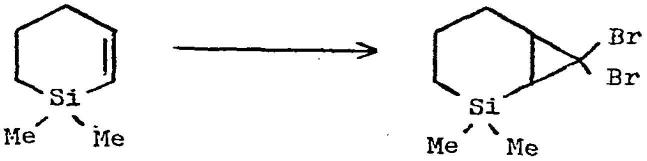
However, the very stable $PhHgCF_3$ is preferable as a CF_2 reagent to the light-sensitive CF_3HgI. Full details have been published concerning the preparation of $Hg(CH_2I)_2$ and $Hg(CH_2Br)_2$ via the respective $XZnCH_2X$ reagents (82). This much more easily effected synthesis of these reagents should enhance their applicability as CH_2 transfer agents.

The reaction of $PhHgOCMe_3$ with dichloromethane gave $PhHgCCl_2H$ in 50% yield (83), and the action of chloroform and the lithium salt of t-buyl hydroperoxide on phenylmercuric chloride gave $PhHgCCl_3$ (84).

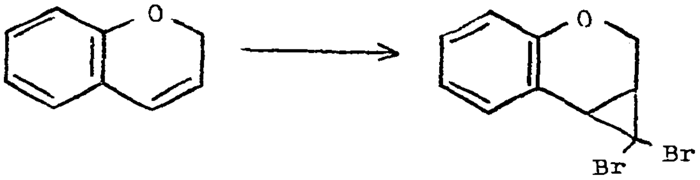
Phenyl(trihalomethyl)mercury and related compounds have found further application in organic synthesis. Phenyl(tribromomethyl)mercury was used to effect the following conversions:



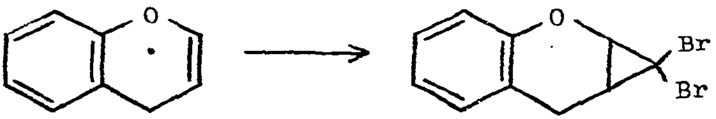
(ref. 85)



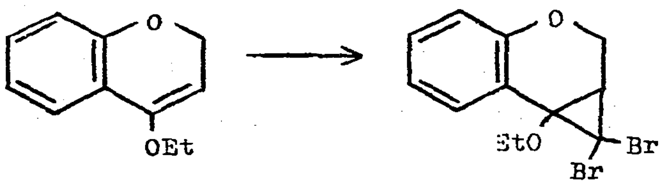
(ref. 86)



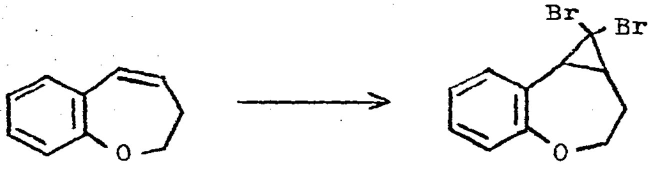
(ref. 87)



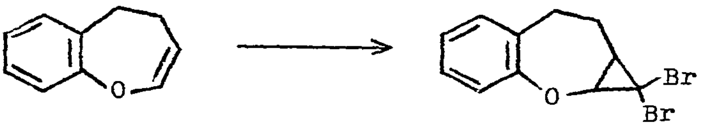
(ref. 87)



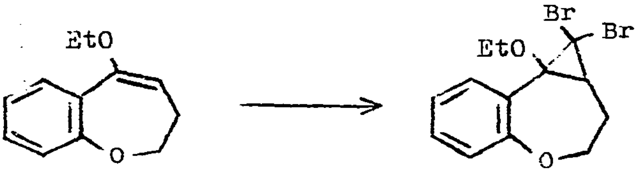
(ref. 87)



(ref. 87)

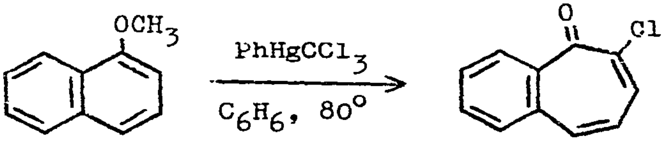


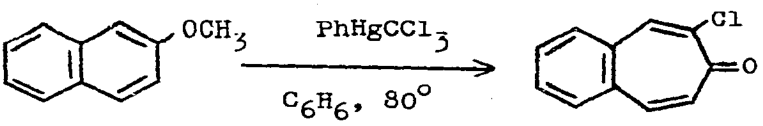
(ref. 87)



(ref. 87)

The reaction of phenyl(trichloromethyl)mercury with 1- and 2-methoxynaphthalene gave tropone derivatives (88):

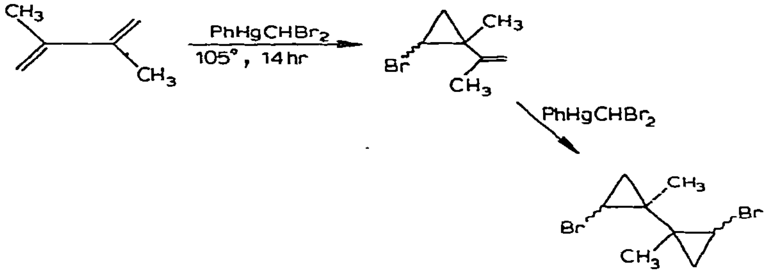




The results of a relative rate study of CCl_2 addition via $PhHgCCl_2Br$ to silyl-olefins of type $Me_n(t\text{-}BuO)_{3-n}SiCH{=}CH_2$

were rationalized in terms of the operation of $d_{\pi}-p_{\pi}$ bonding in the Si-CH=CH_2 system (89).

The application of phenyl(dichloromethyl)mercury and phenyl(bromochloromethyl)mercury in monochlorocyclopropane synthesis has been studied in greater detail (90). As Table VII shows, PhHgCHClBr is a CHCl transfer agent of moderate utility. The CHCl transfer to olefins is a stereospecific process, but free monochlorocarbene does not appear to be involved as an intermediate. Phenyl(dibromomethyl)mercury has been used to add CHBr to 2,3-dimethyl-1,3-butadiene (91):

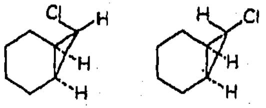
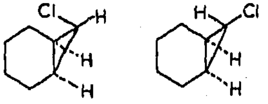
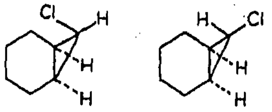
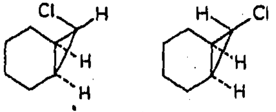
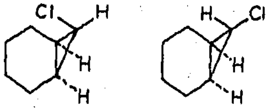


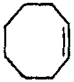
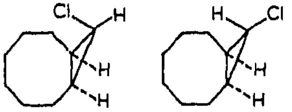
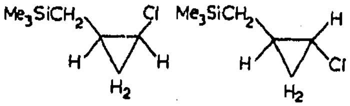
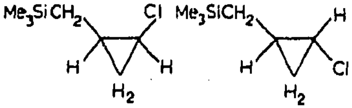
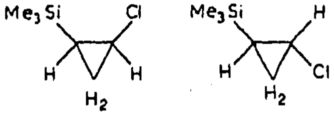
Divalent carbon insertion into single bonds (via organomercury reagents) also has received continued study.

Among the most reactive of single bonds toward divalent carbon reagents is the Si-H linkage. An insertion process (rather than an alkylation-reduction or reduction-alkylation sequence) has been demonstrated for the preparation of methyl silicon compounds from silicon hydrides by reaction with $Hg(CH_2I)_2$ (82). This was shown by a reaction of equimolar quantities of Et_3SiD and Bu_3SiH with $Hg(CH_2I)_2$. The only products which were obtained were Et_3SiCH_2D and Bu_3SiCH_3. The kinetic isotope effect, k(Si-H)/k(Si-D), for the reaction of tri-n-butylsilane with $PhHgCCl_2Br$ was determined to be 1.23 (92).

TABLE VII

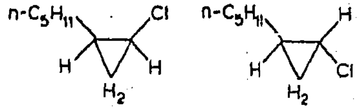
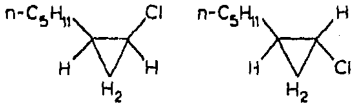
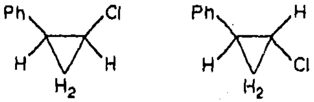
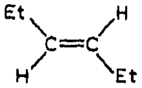
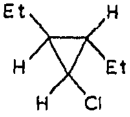
REACTIONS OF PhHgCHClBr AND $PhHgCHCl_2$ WITH OLEFINS (ref. 90)

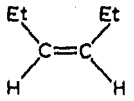
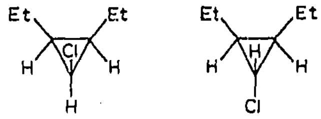
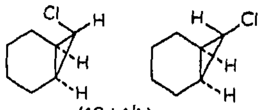
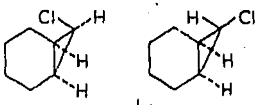
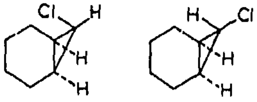
Olefin (mmoles)	Mercurial (mmoles)	Solvent (ml)	Reaction temperature (°C)	Reaction time	Yield of PhHgBr (%)	Cyclopropane products (% Yield ; isomer ratio)
(A) With PhHgCHClBr						
 (200)	20	None	~ 84	6 days	81	 (63 ; 1.3/1)
 (200)	20	None	~ 84	3 days	42	 (29 ; 1.3/1)
 (60)	20	C_6H_6 (10)	~ 84	3 days	18	 (10 ; 1.3/1)
 (60)	20	C_6H_6 (5)	~ 84	6 days	46	 (37 ; 1.3/1)
 (23)	5.6	PhCl (20)	~123	70 h	88	 (59 ; 1.22/1)

 (169)	5.6	None	~140	5 h	94	 (90; 2.1/1)
$Me_3SiCH_2CH{=}CH_2$(26)	4.9	*o*-Xylene (20)	~130	18 h	80	 (62 ; 1.60)
$Me_3SiCH_2CH{=}CH_2$(35)	4.9	None	~140	4 h	74	 (55 ; 2.30)
$Me_3SiCH{=}CH_2$(18)	4.9	C_6H_6 (3)	~130	30 h	35	 (10; 0.6/1)

(Table continued)

TABLE VII (contd.)

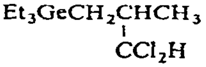
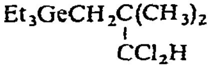
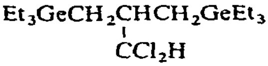
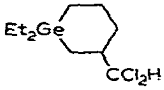
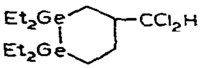
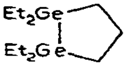
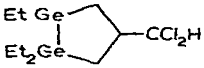
Olefin (mmoles)	Mercurial (mmoles)	Solvent (ml)	Reaction temperature (°C)	Reaction time	Yield of PhHgBr (%)	Cyclopropane products (% yield; isomer ratio)
n-$C_5H_{11}CH{=}CH_2$ (36)	7.4	PhCl (20)	~123	45 h	42	 (23 ; 1.86/1)
n-$C_5H_{11}CH{=}CH_2$ (28)	4.9	None	~135	20 h	50	 (26 ; 1.75/1)
$C_6H_5CH{=}CH_2$ (26)	4.9	PhCl (15)	~135	24 h	69	 (28 ; 1.46/1)
 (48)	4.9	None	~135	18 h	92	 46

 (36)	4.9	None	~140	2 h	88	 (49 ; 3.9/1)
 (200)	20	None	~84	7 days	19	 (16 ; 1/1)
 (100)	21	None	~140	60 h	95	 (57;1.1/1)
 (200)	15	None	~84	8 days		 (8 ; 1/1.2)

To the previously reported examples of β-metal activated CCl_2 insertion into C-H bonds in alkylmetal compounds (OCR-B, 8 (1971) 454-458) have been added some reactions with organogermanium compounds; PhHg CCl_2Br was the CCl_2 source (93) (Table VIII).

TABLE VIII

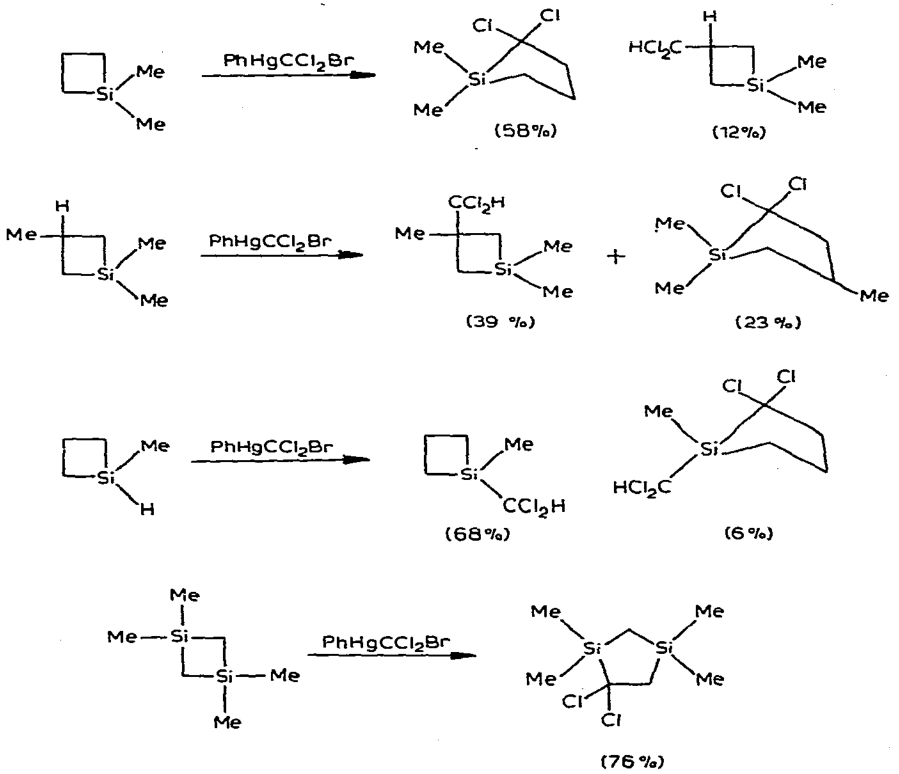
CCl_2 INSERTION PRODUCTS FROM TETRAALKYLGERMANES (via $PhHgCCl_2Br$)

Starting compound	Insertion product	
	Structure	Yield (%)
$Et_3GeCH_2CH_2CH_3$	 $Et_3GeCH_2CH(CCl_2H)CH_3$	41
$Et_3GeCH_2CH(CH_3)_2$	 $Et_3GeCH_2C(CCl_2H)(CH_3)_2$	91
$Et_3GeCH_2CH_2CH_2GeEt_3$	 $Et_3GeCH_2CH(CCl_2H)CH_2GeEt_3$	61
		71
		85
		64

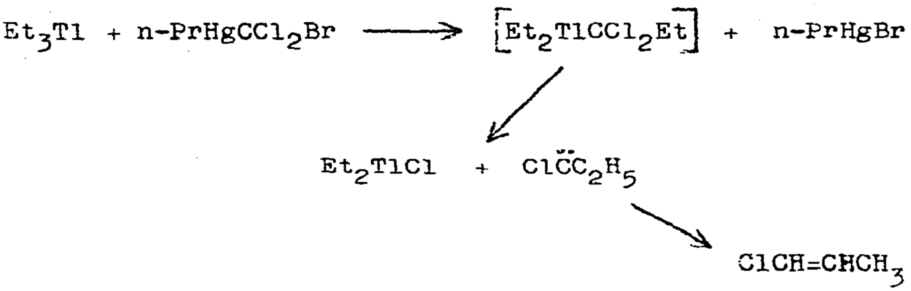
The results of a competition between $i\text{-}BuSiEt_3$ and $i\text{-}BuGeEt_3$ for a deficiency of $PhHgCCl_2Br$ gave k(Ge)/k(Si) = 1.35 for this metal activation which is best explained in terms of metal-carbon bond hyperconjugation.

A reinvestigation of the insertion of CCl_2 (via $PhHgCCl_2Br$) into the benzylic C-H bond of optically active sec-butylbenzene showed that this reaction proceeded with retention of configuration at carbon, which is in harmony with the suggested transition state for CCl_2 insertion into the C-H bond (OCR-B, 8 (1971) 451).

Full details have been published concerning the reactions of $PhHgCCl_2Br$ with silacyclobutanes and a 1,3-disilacyclobutane (95). The observed CCl_2 insertions into Si-C bonds are very unusual, and the fact that they occur no doubt is due to the ring strain of the SiC_3 cycle. The reactions described include the following:

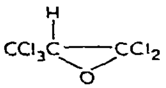


Several different reactions appeared to be involved in the exothermic interaction of n-$PrHgCCl_2Br$ and triethylthallium (75). The presence of 1-chloropropene in the product mixture suggested that some CCl_2 insertion into the Tl-C bond had occurred:

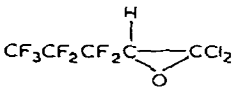


$$Et_3Tl + n\text{-}PrHgCCl_2Br \longrightarrow [Et_2TlCCl_2Et] + n\text{-}PrHgBr$$
$$[Et_2TlCCl_2Et] \longrightarrow Et_2TlCl + Cl\ddot{C}C_2H_5 \longrightarrow ClCH{=}CHCH_3$$

More has been reported on the addition of $PhHgCCl_2Br$-derived dichlorocarbene to the C=O bonds of ketones and aldehydes. Stable oxiranes, $\boxed{15}$ and $\boxed{16}$, were obtained by reaction of

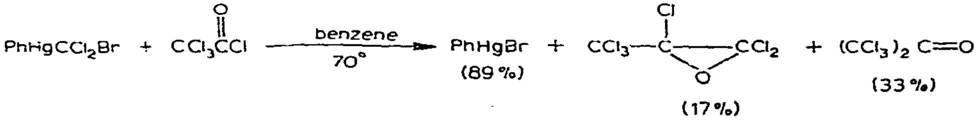


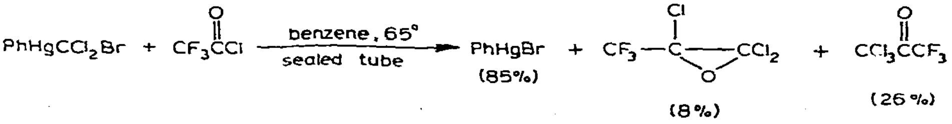
$\boxed{15}$



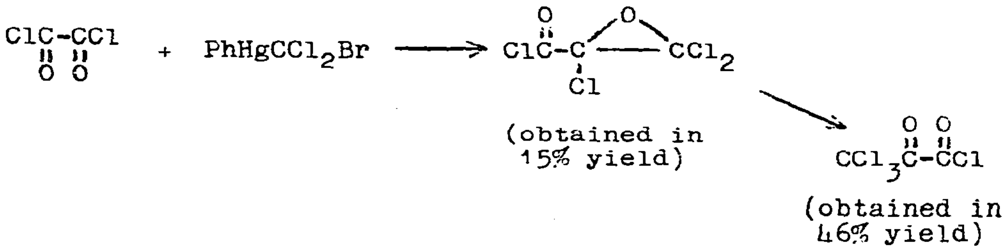
$\boxed{16}$

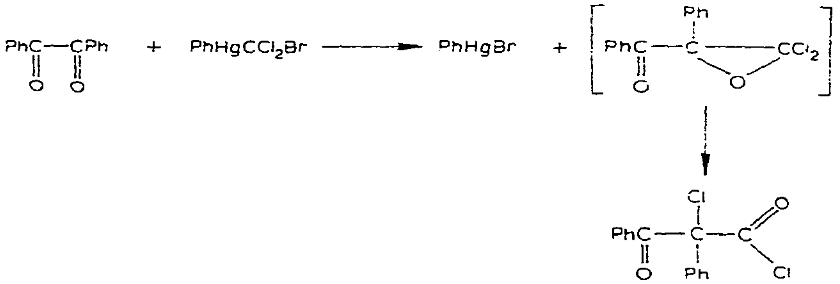
this mercurial with $CCl_3CH{=}O$ and $n\text{-}C_3F_7CH{=}O$, respectively (96). In the case of acyl chlorides derived from trihaloacetic acids, the expected oxiranes were isolated, but the major products were the ketones which presumably were formed in their thermal rearrangement (96):



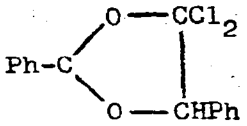


Also studied were reactions of $PhHgCCl_2Br$ with α-dicarbonyl compounds. Here also the initially formed oxiranes were not very stable (96):





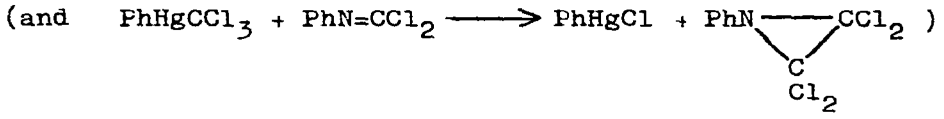
The reaction of $PhHgCCl_2Br$ with benzophenone does not give a stable oxirane. The products of this reaction were found to be $Ph_2ClCCOCl$, Ph_2CCl_2 and carbon monoxide (97). It was suggested that a carbonyl ylide, $Ph_2C{=}\overset{+}{O}{-}\overset{-}{C}Cl_2$, may be the intermediate responsible for the formation of these products. Furthermore, ir spectroscopic evidence in favor of a $PhHgCCl_2Br$-benzophenone complex was presented ($\Delta\nu$ (C=O) of $-16\ cm^{-1}$), and on the basis of this observation, it was postulated that the $PhHgCCl_2Br$-benzophenone reaction does not proceed via free CCl_2. However, subsequent experiments did not provide support for this idea (98). The reaction of $PhHgCCl_2Br$ with benzaldehyde proceeded in similar manner, giving CO, $PhCHCl_2$, and $\boxed{17}$. Here also a carbonyl ylide intermediate was suggested (98).



17

Aryl azides were found to react with $PhHgCCl_3$ as follows (99):

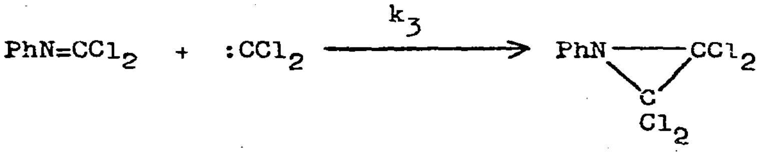
$$PhHgCCl_3 + PhN_3 \xrightarrow{DME,\ 80^{\circ}} PhN{=}CCl_2 + PhHgCl + N_2$$



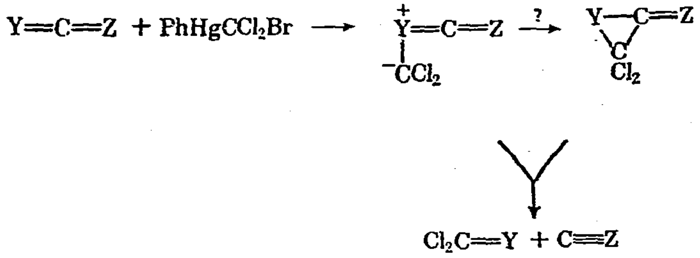
A rate study of this reaction was consistent with the scheme shown below. (For reactions of $PhHgCCl_2Br$ with $RN{=}CCl_2$, see OCR-B, 8 (1971) 450).

$$PhHgCCl_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PhHgCl + :CCl_2$$

$$PhN_3 + :CCl_2 \xrightarrow{k_2} PhN{=}CCl_2 + N_2$$



The reactions of $PhHgCCl_2Br$ with various heteroatom cumulenes provided examples of interesting fragmentation processes (100), summarized in a generalized way as follows:

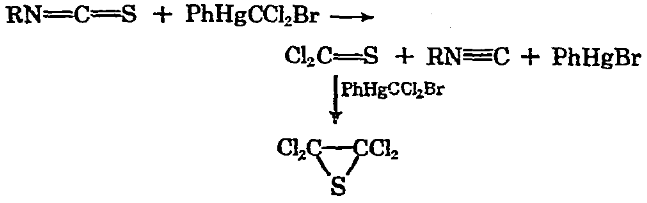


Such behavior was found with:

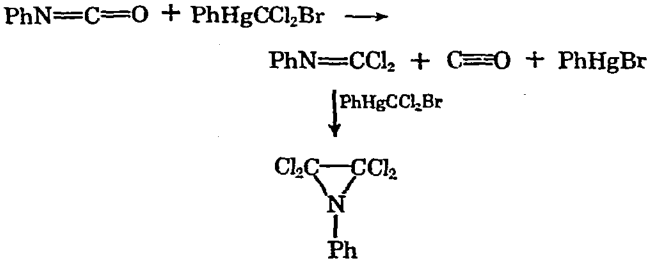
Carbodiimides:

$$\mathrm{Me_2CHN{=}C{=}NCHMe_2 + PhHgCCl_2Br \longrightarrow}$$
$$\mathrm{Me_2CHN{=}CCl_2 + Me_2CHN{\equiv}C + PhHgBr}$$

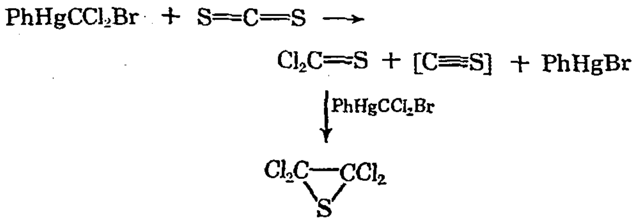
Isothiocyanates:



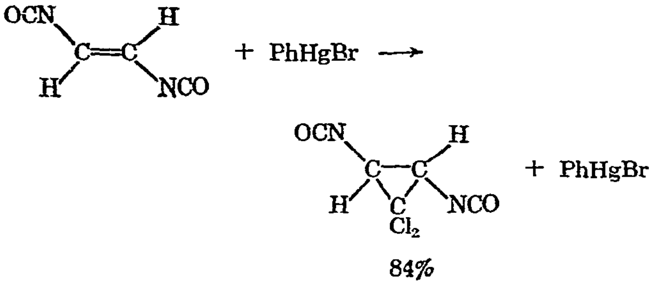
Isocyanates:



Carbon disulfide:



Phenyl isocyanate was rather unreactive toward $PhHgCCl_2Br$, and olefinic isocyanates reacted with this mercury reagent to form cyclopropanes (100):



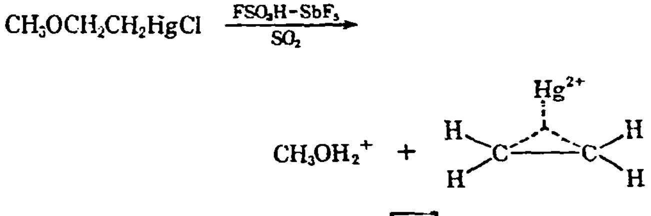
Finally, to end this section on a humorous note, chemists who have prepared and used phenyl(trihalomethyl)-mercury reagents will be amused to learn that these compounds have been patented for application as plant defoliants (101). Included in the list of compounds claimed to be effective are $PhHgCBr_3$, $PhHgCF_3$, $p\text{-}BuC_6H_4HgCCl_2Br$, as well as some patent attorney's flights of fancy such as CBr_3 $HgCCl_2CCl_3$, $PhHgCBr_2CBr_3$, $PhHgCCl_2CI_3$ and $BuHgCI_2CI_3$!

4. MERCURATION OF UNSATURATED COMPOUNDS

A. OLEFINS AND ACETYLENES

The most exciting new development in the area of olefin solvomercuration is the generation and identification of stable mercurinium ions by Olah and Clifford. Mercurinium ions had long been postulated as intermediates in the solvomercuration of olefins, but all previous claims of their spectroscopic characterization had turned out to be incorrect.

In highly acidic media such as FSO_3H-SbF_5-SO_2 at low temperatures, 2-methoxyethylmercuric chloride was found to react as follows (102):



$\boxed{18}$

The ^{1}H nmr spectrum of this reaction mixture, in addition to signals due to $CH_3OH_2^+$, showed a singlet at δ 7.68 with $J(^{199}Hg-^1H) = 190Hz$. This signal was attributed to the ethylenemercurinium ion, $\boxed{18}$,* Treatment of such a solution

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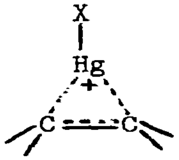
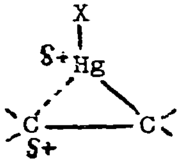
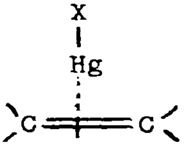
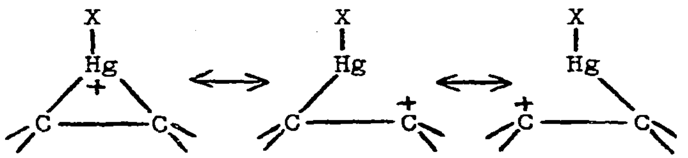
* The structure $\boxed{18}$ represents Olah's way of depicting the mercurinium ion, but we note it is only one of many which have appeared in the literature:



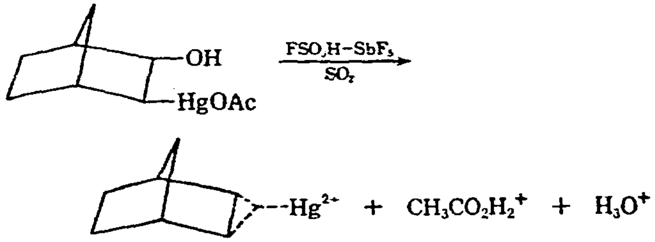




and

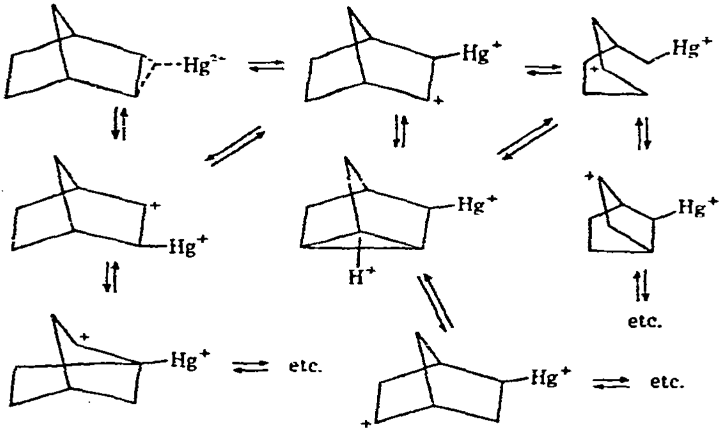


with an excess of toluene, followed by reduction with NaBH$_4$ gave p-CH$_3$C$_6$H$_4$C$_2$H$_5$. The norbornylenemercurinium ion was generated in similar manner at -70° (102):

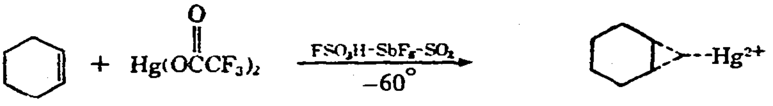


$\boxed{19}$

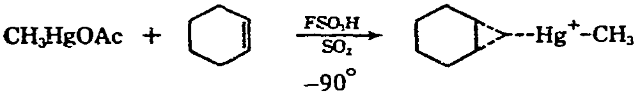
Norbornylene was obtained when such solutions were quenched with water, norbornane when they were treated with NaBH$_4$. Nmr studies indicated that $\boxed{19}$ equilibrated (reversibly) on being warmed to -30° in FSO$_3$H-SbF$_5$-SO$_2$ solution:



Mercurinium ions also could be formed by direct mercuration of olefins in strongly acid media (103):



This procedure made accessible methylmercurinium ions as well:



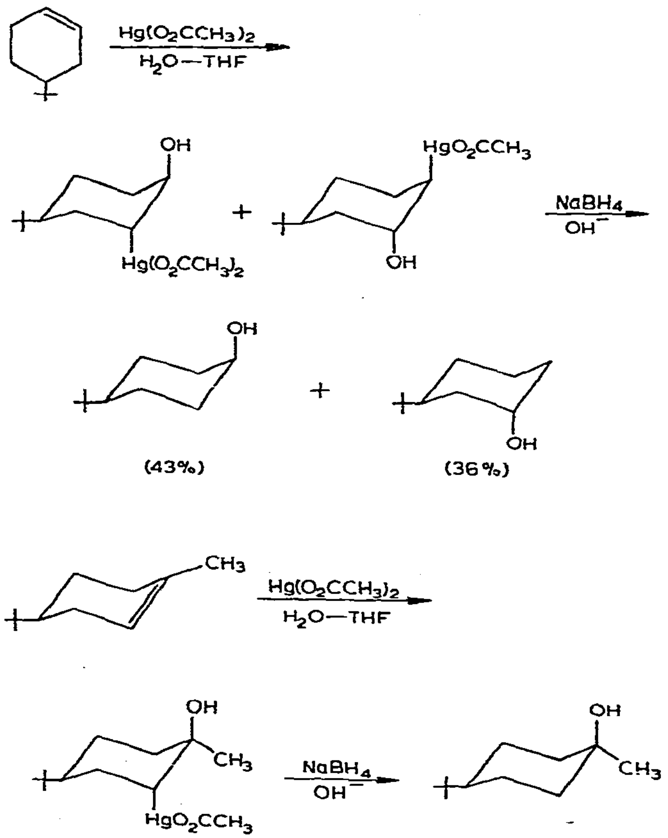
At -60°, the equilibrium process shown below could be distinguished by nmr spectroscopy.

It should be emphasized, however, that if mercurinium ions are observed as primary products of the interaction of olefins and mercuric salts in such highly acidic media at low temperatures, it does not necessarily follow that such mercurinium ions are intermediates in the solvomercuration of the same olefins under completely different reaction conditions.

A study of the cis-oxymercuration of trans-cyclooctene and norbornene (the effect of added salts) provided results which were interpreted as being in favor of the intermediacy of a mercurinium ion and against a 4-center mechanism (104). On the other hand, work by Brown and Liu (105) on the cis-oxymercuration of the strained norbornene and 7,7-dimethylnorbornene (relative ratio for exo addition, k(exo-norbornyl)/ k(7,7-dimethyl-exo-norbornyl)) seemed to exclude the operation of a cyclic mechanism and an intermediate mercurinium ion. These authors stressed the apparent unimportance of the mercurinium ion under the usual oxymercuration conditions (105).

An interpretation of the mercuration of the C=C bond in terms of the hard-soft acid-base concept has been published (106).

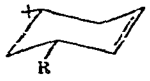
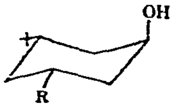
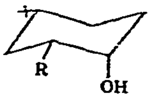
The oxymercuration of 4-tert-butylcyclohexene and 1-methyl-4-tert-butylcyclohexene was found to give trans-diaxial products (107):



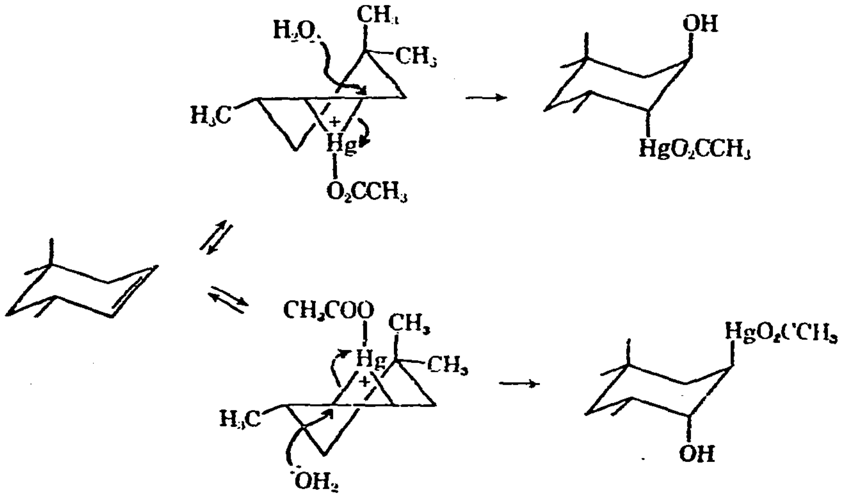
After comparison of this result with those of the bromination, methoxybromination and hydrobromination of the same olefins, it was concluded by Pasto and Gontarz that the oxymercuration of these cyclohexenes proceeds by way of mercurinium ion intermediates which are formed in fast, reversible pre-rate determining equilibria. In related studies, the same authors found that the dominant steric effect operative in the oxymercuration of such substituted cyclohexenes involves torsional angle effects which are a function of the size of the alkyl group in cis-3-alkyl-5-tert-butylcyclohexenes (Table IX) (108).

TABLE IX

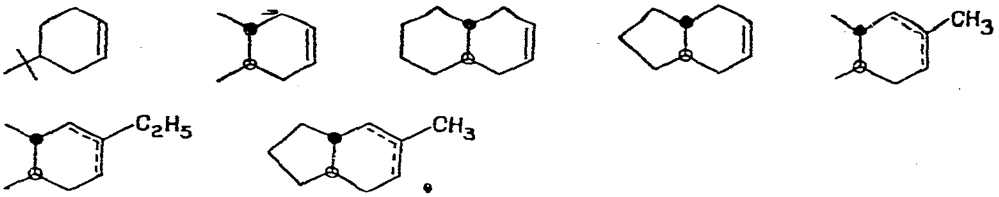
RESULTS OF OXYMERCURATION–REDUCTIVE DEMERCURATION OF *cis*-3-ALKYL-5-*tert*-BUTYLCYCLOHEXENES AT 25° (108)

 R=		
H	46.4	53.6
CH_3	89.8	10.2
C_2H_5	90.5	9.5
$CH(CH_3)_2$	94.2	5.8
$C(CH_3)_3$	99.06	0.94

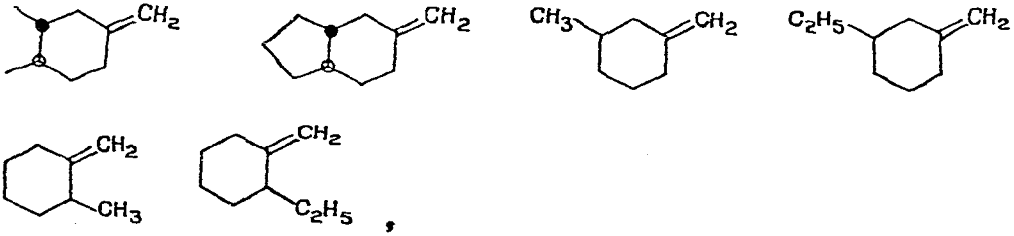
The process leading to the observed oxymercuration products is pictured as shown below for the oxymercuration of 3,5,5-trimethylcyclohexene.



A very similar study was reported by French workers (109). For the endocyclic substituted cyclohexenes,

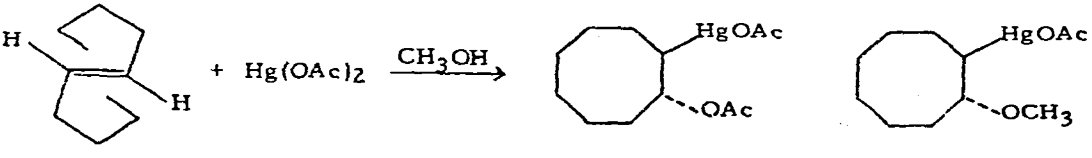


the oxymercuration/$NaBH_4$ reduction sequence gave $>$ 95-99% of the axial alcohol. For exocyclic olefins,



the reaction was less stereospecific, with alkyl substituents in the 3 position favoring formation of the axial alcohol and alkyl groups in the 2 position favoring formation of the equatorial alcohol.

In the oxymercuration of trans-cyclooctene, two products are formed:



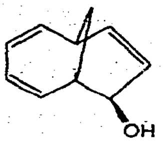
20 21

Which one is formed depends on the presence of other ligands that can bond covalently to mercury, either added salts (104) or more nucleophilic solvents (110), with the acetoxy compound $\boxed{20}$ being favored in the presence of added salts or more nucleophilic solvents. The rate of racemization of (+)-$\boxed{21}$, obtained from (-)-trans-cyclooctene, in solution, depended upon the nature of the solvent, with racemization being faster in the more nucleophilic solvents (110).

In terms of more preparatively oriented oxymercuration chemistry, one may note the following reports.

The preparation of optically active alcohols was achieved via the oxymercuration-demercuration sequence using chiral mercuric carboxylates in place of the usual mercuric acetate (111). Thus, the conversion of 1-decene to 2-decanol via reaction with mercuric (+)-tartrate followed by $NaBH_4$ reduction gave product with 17.4% enantiomeric excess ((-) isomer). A similar sequence carried out with mercuric (+)-lactate gave 2-decanol with 2.3% enantiomeric excess ((-) isomer).

The oxymercuration of bullvalene followed by reduction of the mercuration product with $NaBH_4$ was reported to give $\boxed{22}$ (112) (cf. OCR-B, 8 (1971) 468 for a previous report of this reaction). The solvomercuration of cis, cis-1,5-cyclooctadiene, reported by two groups last year (OCR-B, 8 (1971) 465, 467) has been reported by a third group to give $\boxed{23}$ in methanol and $\boxed{24}$ in acetic acid solution, as part of a comprehensive study of olefin reactivity (113). Hydroxymercuration of 1-methylcyclobutene by mercuric perchlorate in dilute $HClO_4$ solution gave the oxymercuration product $\boxed{25}$, which, however, decomposed in strong acid solution to give as final products mercury and methyl cyclopropyl ketone (114).



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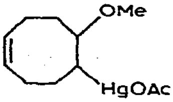

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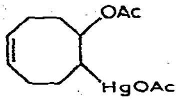

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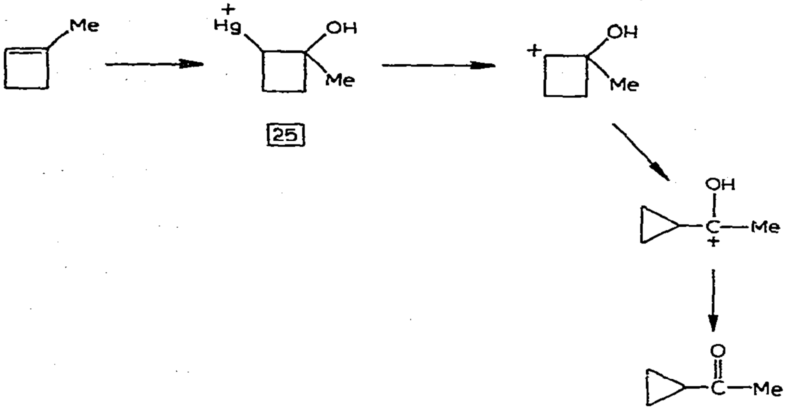
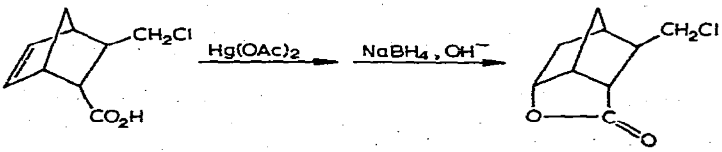


25

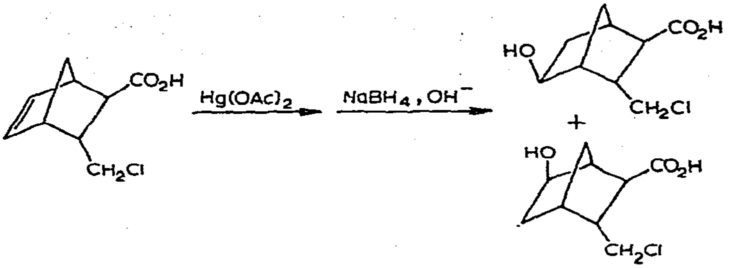
The methoxymercuration of pendant vinyl groups in cross-linked divinylbenzene polymers and styrene-divinylbenzene copolymers has been reported at a polymer symposium (115). These heterogeneous reactions proceed much more slowly than oxymercurations in solution, but they do go to complete conversion.

Oxymercuration of functional olefins, in particular, those with functional groups which take part in the reaction, are of interest.

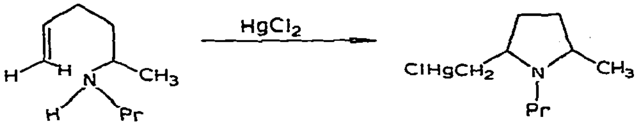
In carboxy-substituted norbornenes, the disposition of the carboxy group is of importance (116):

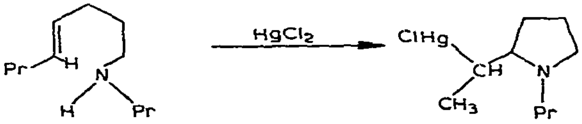


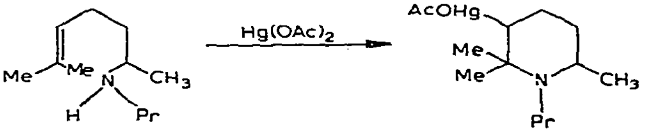
but:

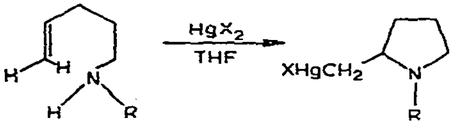


Cyclization of unsaturated amines was accomplished via the mercuration-reduction sequence (117, 118):

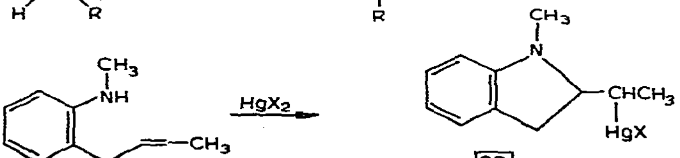








R = H , X = OAc , 70 %
R = Me , X = OAc, 50 %
R = n-Pr , X = Cl , 75 %
R = t-Bu , X = Cl , 60 %
R = Ph , X = Cl , 0 %



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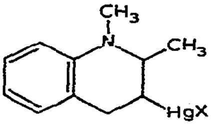

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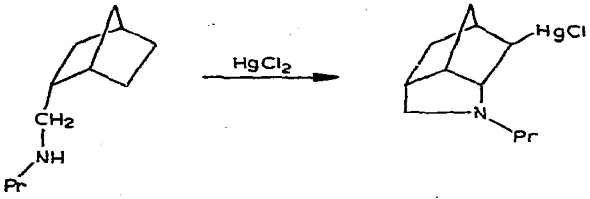
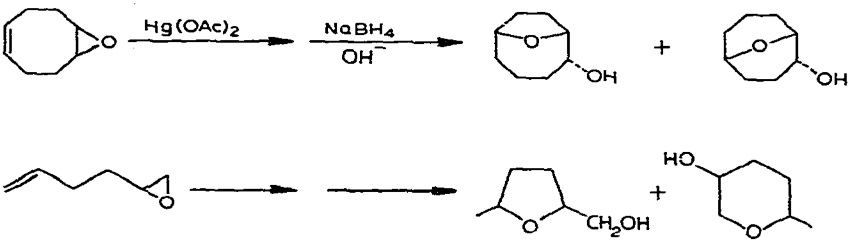
(The ratio of $\boxed{26}$ to $\boxed{27}$ obtained depends on the mercuric salt and on the solvent used).

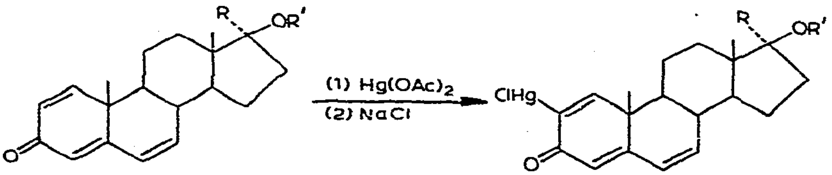


Diene monoxides have been subjected to the mercuration-$NaBH_4$ reduction sequence (119), and neighboring group participation by oxirane oxygen was found to occur:



A rate acceleration due to this participation was observed. Some relative rate data for oxymercuration of various C_8 cyclic olefins are given in Table X (119).

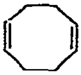
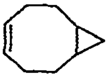
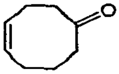
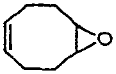
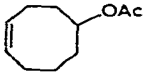
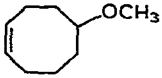
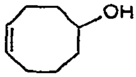
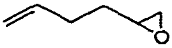
Full details of the mercuration of steroidal 3-keto-1,4,6-trienes (OCR-B, 6 (1970) 273) have been reported (120).



R = Me, R' = H
and
R = H, R' = EtCO

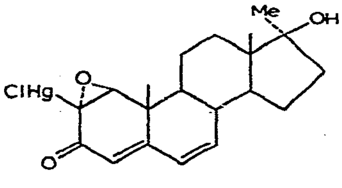
TABLE X (119)

RELATIVE RATES OF OXYMERCURATION AT 25°

Compound	Relative rate [b]	Time sec. [c]
	0.0005	7200
		15
	0.02	60
		840
	1.0	5
		5650
		1680
		2
	1.1	
	3.3	
	0.92	90

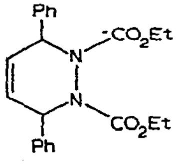
[a] Reaction run in 50% THF–water, unless otherwise specified. [b] From competition reactions; precision is about ±20%. [c] Time required for decolorization of mercuric complex in THF–water.

The R = Me, R' = H compound was epoxidized with 30% H_2O_2 to $\boxed{28}$

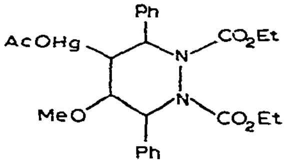


$\boxed{28}$

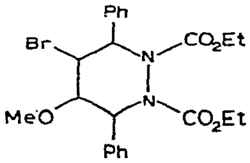
The methoxymercuration of $\boxed{29}$ gave $\boxed{30}$ (121). $\boxed{29}$ was rather unreactive, and the highly active mercuric perchlorate had to be used in order to obtain a satisfactory rate of reaction. Brominolysis of $\boxed{30}$ gave $\boxed{31}$.



$\boxed{29}$

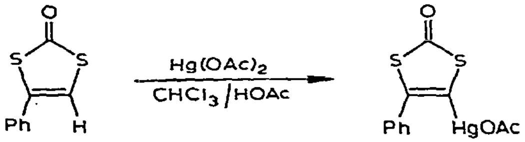


$\boxed{30}$

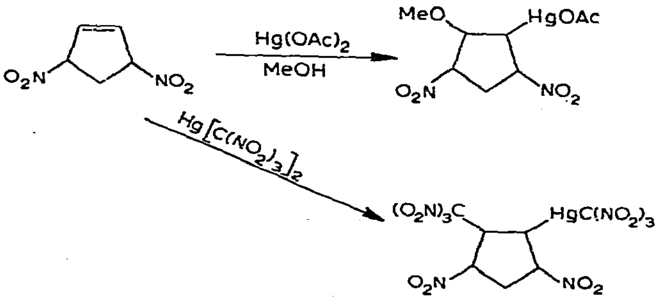


$\boxed{31}$

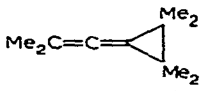
Also reported has been the mercuration of 4-phenyl-1,3-dithiolene-2-one (122):



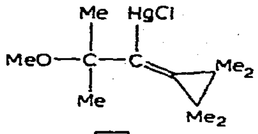
3,5-Dinitro-1-cyclopentene was mercurated by Russian workers (123):



Several papers have been devoted to the oxymercuration of allenes. The methoxymercuration of $\boxed{32}$ gave $\boxed{33}$ (124). The

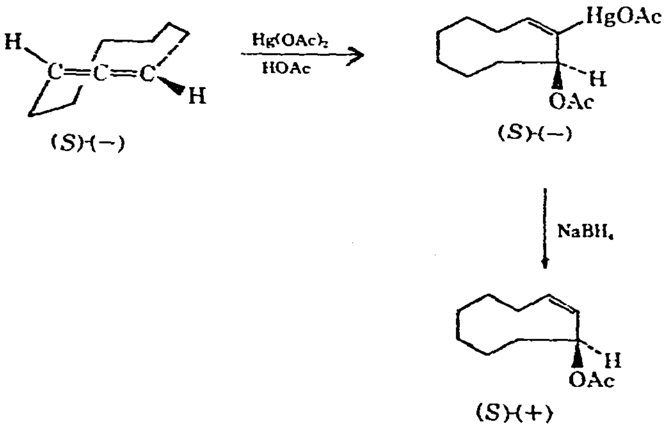


$\boxed{32}$



$\boxed{33}$

chloromercuri group of $\boxed{33}$ was readily replaced by bromine via brominolysis in pyridine solution, but the action of $NaBH_4$ in aqueous NaOH on $\boxed{33}$ was anomalous, giving the symmetrization product, the diorganomercurial, instead of the expected reduction product. Reaction of $\boxed{33}$ with $LiAlH_4$ regenerated allene $\boxed{32}$. The acetoxymercuration of optically active 1,2-cyclononadiene gave an optically active mercurial (125):



The absolute configuration of 1,2-cyclononadiene was determined during the course of this study. Indian workers (126) have reported methoxymercuration (using $HgCl_2$)-demercuration of 1,2-cyclononadiene, 1,2-cyclodecadiene, 1,2-undecadiene and 1,2-tridecadiene. The first two allenes gave the cis-oxymercurial; the second two, the trans-oxymercurial. The results of the $NaBH_4$ reduction of these products are shown in Table XI.

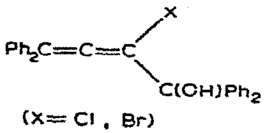
TABLE XI

SODIUM BOROHYDRIDE REDUCTION OF CYCLIC VINYLIC ORGANOMERCURIALS (126)

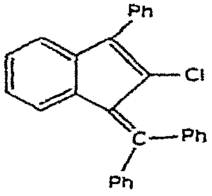
Compound	Product(s)	Yield (%)
cis-$C_{10}H_{17}OHgCl$	3-methoxycyclononene (*cis*, 100%)	72
cis-$C_{11}H_{19}OHgCl$	3-methoxycyclodecene (*cis*, 78%; *trans*, 22%)	54
trans-$C_{12}H_{21}OHgCl$	3-methoxycycloundecene (*cis*, 15%; *trans*, 85%)	80
trans-$C_{14}H_{25}OHgCl$	3-methoxycyclotridecene (*cis*, 15%; *trans*, 85%)	76

In view of the proven radical mechanism of $NaBH_4$ reduction of organomercurials, the formation of both cis and trans products is not surprising.

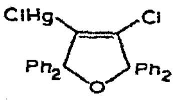
The reaction of $\boxed{34}$ (X = Cl) with $HgCl_2$ in acetone gave $\boxed{35}$ as major product. In t-butanol solution, on the other hand, $\boxed{34}$ (X = Cl) reacted with mercuric chloride to give $\boxed{36}$, with mercuric bromide to give $\boxed{37}$. The bromo compound $\boxed{34}$ reacted with mercuric bromide in t-butanol to produce $\boxed{38}$, with mercuric chloride to give $\boxed{37}$. Demercuration of $\boxed{36}$, $\boxed{37}$, and $\boxed{38}$ with $NaBH_4$ replaced the halomercuri groups with a hydrogen atom. The mechanisms of these mercuration reactions were discussed.



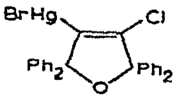
$\boxed{34}$



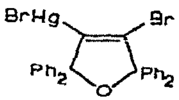
$\boxed{35}$



$\boxed{36}$

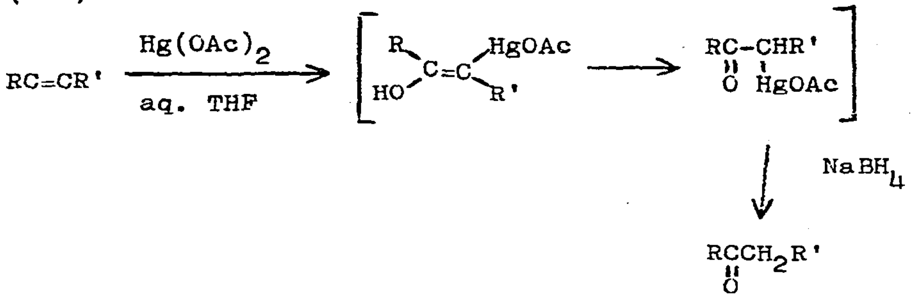


$\boxed{37}$

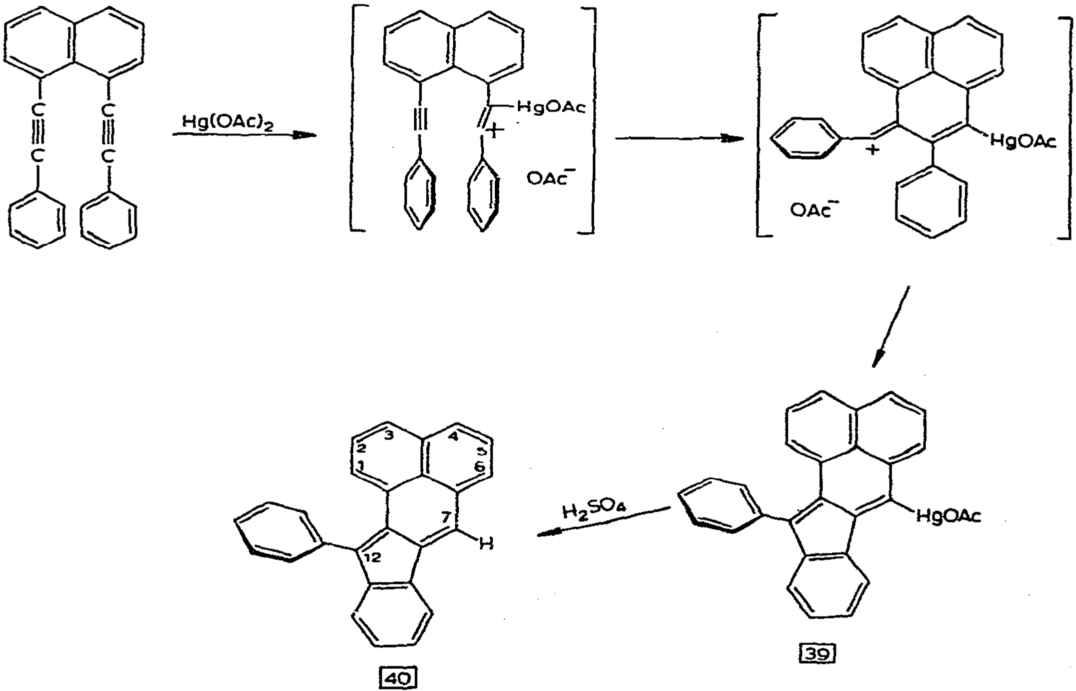


$\boxed{38}$

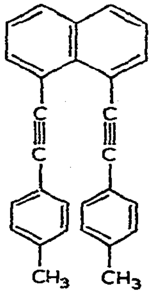
Some studies of the oxymercuration of acetylenes also have been reported. Oxymercuration of 1-octyne, 3-hexyne, cyclotridecyne and phenylacetylene, followed by treatment of the mercurials formed with $NaBH_4$ gave ketones in good yield (128):



Diphenylacetylene failed to react under these conditions. Mercuration (with $Hg(OAc)_2$ in methanol) of 1,8-bis(phenylethynyl)naphthalene gave $\boxed{39}$ as final product, presumably via the route shown below (129).



Cleavage of $\boxed{39}$ with sulfuric acid gave $\boxed{40}$, which also was formed more directly by carrying out the mercuration of 1,8-bis(phenylethynyl)naphthalene in HOAc/H_2SO_4 medium. Mercuration of $\boxed{41}$ and $\boxed{42}$ under the latter conditions gave $\boxed{43}$, R = H and R = Me, respectively. However, the action of mercuric acetate in methanol on $\boxed{44}$ resulted in the formation of $\boxed{45}$, since the intermediate vinyl cation could not undergo ring closure.



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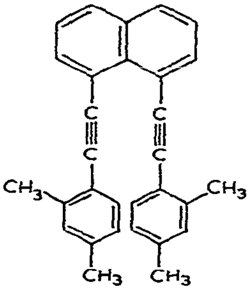

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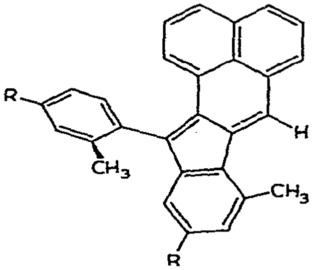
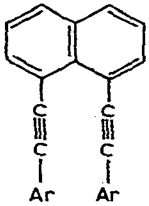


R = H
R = CH_3

43



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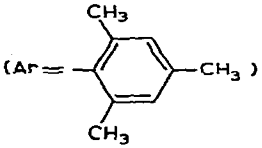
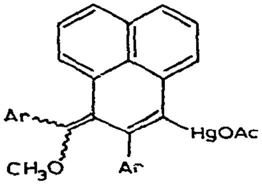
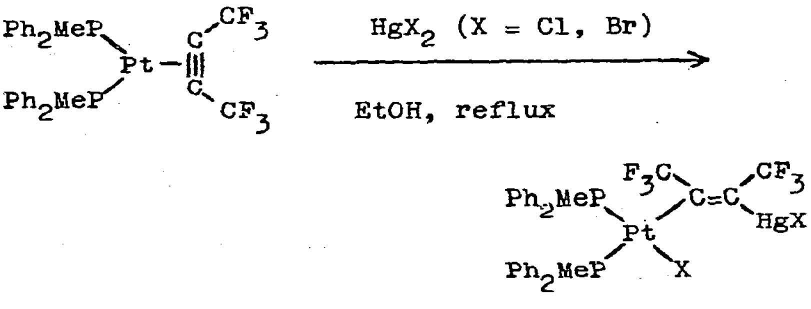


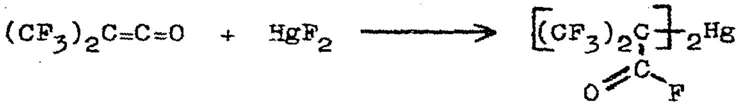


45

Of special interest is an example of the mercuration of a coordinated acetylene (130):



The addition of mercuric fluoride to a ketene has been described (131):

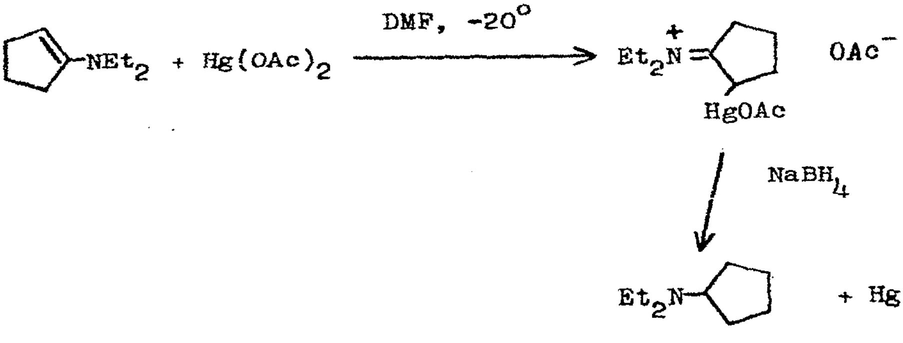


$$(CF_3)_2C{=}C{=}O + HgF_2 \longrightarrow [(CF_3)_2C(C(=O)F)]_2Hg$$

$\boxed{46}$

Treatment of $\boxed{46}$ with sodium carbonate gave a mixture of $[CF_2{=}C(CF_3)]_2Hg$, $CF_2{=}C(CF_3)HgCH(CF_3)_2$ and $[(CF_3)_2CH]_2Hg$.

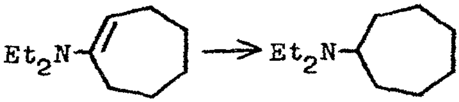
A new tertiary amine synthesis based on the mercuration-demercuration of enamines has been developed (132):



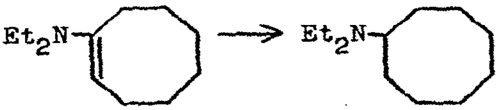
(78%)

Other conversions effected by this sequence were:

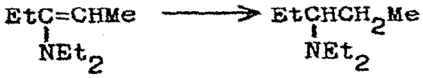
(77%)



(90%)

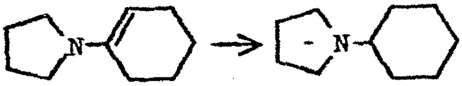


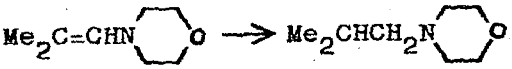
(93%)



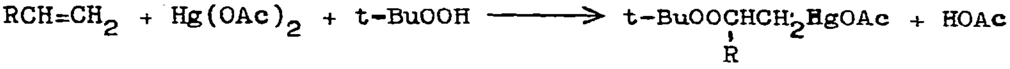
$$EtC(NEt_2){=}CHMe \longrightarrow EtCH(NEt_2)CH_2Me$$

(71%)

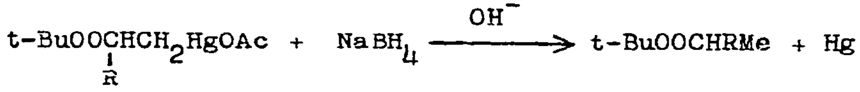




Bloodworth has provided full details of the peroxymercuration of monosubstituted ethylenes, which coupled with reduction of the mercurials formed by $NaBH_4$, constitutes a useful new synthesis of secondary alkyl peroxides (133) (cf. OCR-B, 6 (1970) 265).

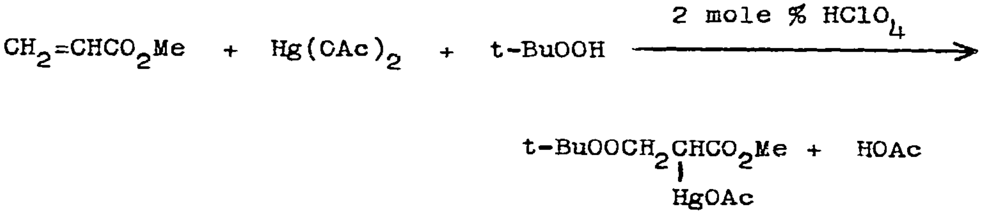


$$RCH{=}CH_2 + Hg(OAc)_2 + t\text{-}BuOOH \longrightarrow t\text{-}BuOO\underset{R}{C}HCH_2HgOAc + HOAc$$



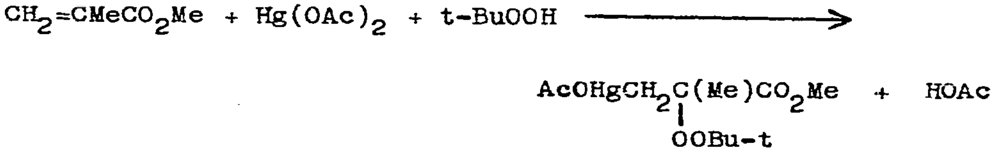
$$t\text{-}BuOO\underset{R}{C}HCH_2HgOAc + NaBH_4 \xrightarrow{OH^-} t\text{-}BuOOCHRMe + Hg$$

This work was extended to the t-butylperoxymercuration of α,β-unsaturated ketones and esters (134). α-Mercuration was found to occur with olefins of type $CH_2{=}CHCOY$, $RCH{=}CHCOY$ and $R_2C{=}CHCOY$ (Y = alkyl or alkoxy):



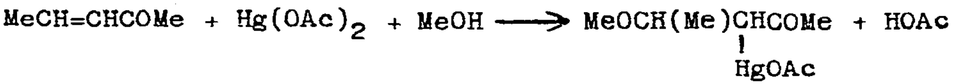
$$CH_2{=}CHCO_2Me + Hg(OAc)_2 + t\text{-}BuOOH \xrightarrow{2\ \text{mole}\ \%\ HClO_4} t\text{-}BuOOCH_2\underset{HgOAc}{C}HCO_2Me + HOAc$$

However, with olefins of type $CH_2{=}CRCOY$, β-mercuration took place:



$$CH_2{=}CMeCO_2Me + Hg(OAc)_2 + t\text{-}BuOOH \longrightarrow AcOHgCH_2\underset{OOBu\text{-}t}{C}(Me)CO_2Me + HOAc$$

This investigation was extended to the methoxymercuration of α,β-unsaturated esters and ketones (134). The same directional effects were observed, e.g.:



$$\mathrm{MeCH{=}CHCOMe + Hg(OAc)_2 + MeOH \longrightarrow MeOCH(Me)\underset{\displaystyle HgOAc}{\underset{|}{C}}HCOMe + HOAc}$$

but

$$\mathrm{CH_2{=}CMeCOMe + Hg(OAc)_2 + MeOH \longrightarrow AcOHgCH_2C(Me)COMe + HOAc}$$

The results reported are summarized in Tables XII, XIII and XIV. In most of the examples given, the organomercury acetate produced initially was converted to the bromide or chloride. Nmr spectroscopy was used extensively in determining the structure of the products.

The kinetics of the methoxymercuration of phenyl cinnamate have been studied (135). A second order reaction was indicated.

TABLE XII

t-BUTYL PEROXYMERCURATION OF αβ-UNSATURATED CARBONYL COMPOUNDS: α-MERCURATION

$\mathrm{R^1R^2C{:}CR^3{\cdot}COY \rightarrow R^1R^2C(O{\cdot}OBu^t){\cdot}CR^3(Hg{\cdot}X){\cdot}COY}$

αβ-Unsaturated carbonyl compd.	R^1	R^2	R^3	Y	Reaction time	Yield (crude) (%)	X	Yield (pure) (%)
But-1-en-3-one (methyl vinyl ketone)	H	H	H	Me	1 hr.	96	Br	50
Methyl propenoate (methyl acrylate)	H	H	H	OMe	10 min.	99	Br	31
trans-Pent-3-en-2-one	H	Me	H	Me	5 min.	97	Br	
trans-Methyl but-2-enoate (methyl crotonate)	H	Me	H	OMe	30 min.	97	Br	58
3-Methylpent-3-en-2-one	H	Me	Me	Me	3 days	30	Cl	25
trans-Methyl 2-methylbut-2-enoate (methyl tiglate)	H	Me	Me	OMe	3 days	10	Br	8
2-Methylpent-2-en-4-one (mesityl oxide)	Me	Me	H	Me	5 min.	97	Br	95
Methyl 3-methylbut-2-enoate (methyl 3,3-dimethylacrylate)	Me	Me	H	OMe	5 min.	99	Br	94
trans-1,3-Diphenylpropenone (chalcone)	H	Ph	H	Ph	1 hr.	98	OAc	75
Chalcone	H	Ph	H	Ph	1 hr.	98	Br	60
trans-Methyl 3-phenylpropenoate (methyl cinnamate)	H	Ph	H	OMe	6 hr.	96	OAc	86
Methyl cinnamate	H	Ph	H	OMe	6 hr.	96	Br	70

TABLE XIII

METHOXYMERCURATION OF αβ-UNSATURATED CARBONYL COMPOUNDS: α-MERCURATION
$R^1R^2C{:}CR^3{\cdot}COY \rightarrow R^1R^2C(OMe){\cdot}CR^3(Hg{\cdot}X){\cdot}COY$

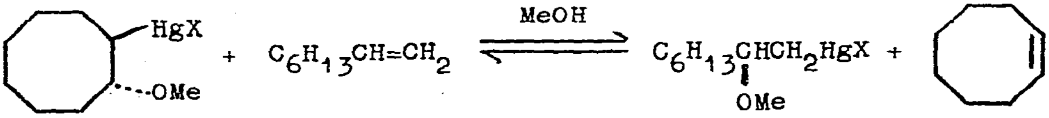
αβ-Unsaturated carbonyl compd.	R^1	R^2	R^3	Y	Reaction time	Yield (crude) (%)	X	Yield (pure) (%)
Methyl vinyl ketone	H	H	H	Me	5 min.	100	Br	25
Methyl acrylate	H	H	H	OMe	4 hr.	90	Br	40
Pent-3-en-2-one	H	Me	H	Me	5 min.	100	Br	73
Methyl crotonate	H	Me	H	OMe	5 min.	100	Br	70
3-Methylpent-3-en-2-one	H	Me	Me	Me	48 hr.	40	OAc	18
Methyl tiglate	H	Me	Me	OMe	24 hr.	57	Br	24
Mesityl oxide	Me	Me	H	Me	15 min.	100	Br	83
Methyl 3,3-dimethylacrylate	Me	Me	H	OMe	1 min.	100	Br	40
Chalcone	H	Ph	H	Ph	3 min.	100	OAc	77
Chalcone	H	Ph	H	Ph	3 min.	100	Br	74
Methyl cinnamate	H	Ph	H	OMe	10 min.	98	OAc	90
Methyl cinnamate	H	Ph	H	OMe	10 min.	98	Br	74

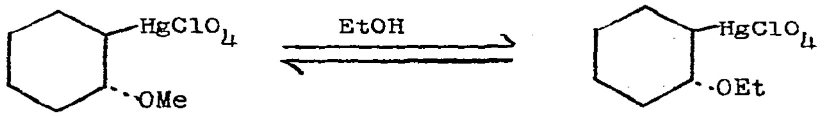
TABLE XIV

METHOXY- AND t-BUTYL PEROXY-MERCURATION OF αβ-UNSATURATED CARBONYL COMPOUNDS: β-MERCURATION
$CH_2{:}CR^3{\cdot}COY \rightarrow XHg{\cdot}CH_2{\cdot}CR^3(OR)COY$

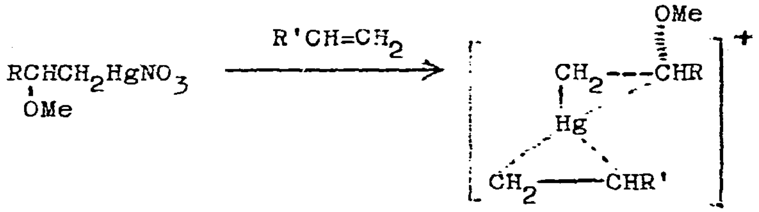
αβ-Unsaturated carbonyl compd.	R^3	Y	R	Reaction time	Yield (crude) (%)	X	Yield (pure) (%)
2-Methylbut-1-en-3-one (methyl isopropenyl ketone)	Me	Me	Me	30 min.	97	Br	30
Methyl isopropenyl ketone	Me	Me	OBu^t	24 hr.	92	OAc	60
Methyl isopropenyl ketone	Me	Me	OBu^t	24 hr.	92	Br	30
Methyl 2-methylpropenoate (methyl methacrylate)	Me	OMe	Me	12 hr.	100	OAc	60
Methyl methacrylate	Me	OMe	Me	12 hr.	100	Br	25
Methyl methacrylate	Me	OMe	OBu^t	12 hr.	97	Br	70
Methyl 2-phenylpropenoate (methyl atropate)	Ph	OMe	Me	12 hr.	50	Br	
Methyl atropate	Ph	OMe	OBu^t	5 days	65	Br	16.5

The kinetics of the displacement of an oxymercurated olefin by a free olefin (transoxymercuration) and of alkoxy exchange reactions involving oxymercurated olefins have been investigated (136). Typical reactions might be:



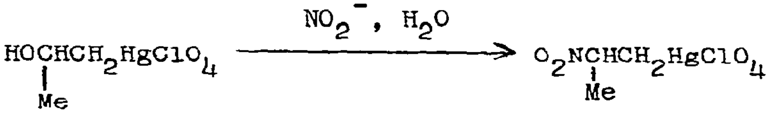


Such reactions proceed best with the more ionic mercurials (perchlorates, nitrates) and are catalyzed by acid. A bis-olefin-mercury cation, $\boxed{47}$, was believed to be involved in the transoxymercuration reaction.



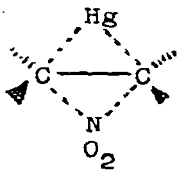
$\boxed{47}$

Other β -substituent exchanges may be noted. Japanese workers have described the conversion of hydroxy- to nitromercurated olefins (137):



$$\mathrm{HO\underset{Me}{C}HCH_2HgClO_4 \xrightarrow{NO_2^-,\ H_2O} O_2N\underset{Me}{C}HCH_2HgClO_4}$$

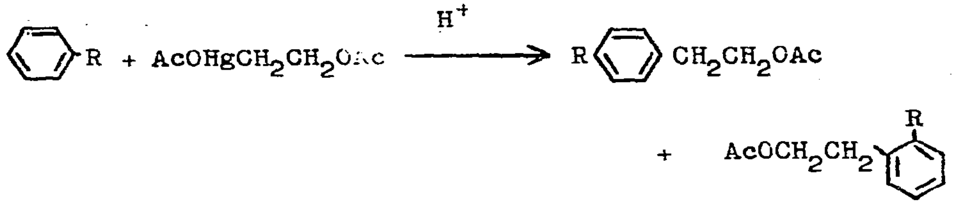
On the basis of rate and stereochemical studies, a mercurinium ion intermediate, $\boxed{48}$, was suggested.



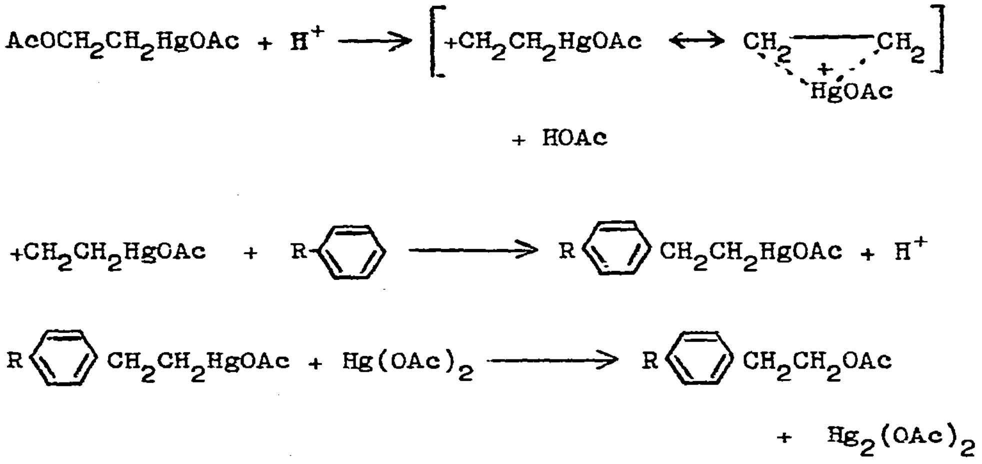
$\boxed{48}$

The decomposition of the methoxymercuration product of allylurea, $H_2NCONHCH_2CH(OMe)CH_2HgCl$ ("Neohydrin", a diuretic) in aqueous solution was found to involve hydroxy for methoxy exchange to give $H_2NCONHCH_2CH(OH)CH_2HgCl$ (138).

The alkylation of substituted benzenes by oxymercurated olefins has been known for some time:



Perchloric acid has been found to catalyze this reaction and the following reaction course was suggested (139):



$$Hg_2(OAc)_2 \xrightarrow{(HClO_4)} Hg(OAc)_2 + Hg$$

Thermal and photochemical reactions of $n\text{-}C_8H_{17}CH(OAc)CH_2HgOAc$ with benzene and toluene gave moderate yields of aromatic substitution products, but alkyl chain isomerization took place under photochemical conditions (140):

$n\text{-}C_8H_{17}CH(OAc)CH_2HgOAc + C_6H_6 \longrightarrow$

a) thermal reaction:

1-phenyl-2-decene (19%)

b) photochemical:

1-phenyl-1-decene (3.6%); 1-phenyl-2-decene (11.3%);

1-phenyl-3-decene (2.6%); 1-phenyl-4-decene (1.6%).

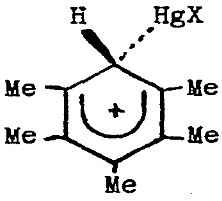
Among miscellaneous items appropriate to this section are the following:

An oxymercuration-demercuration experiment suitable for use in an undergraduate laboratory has been described (141).

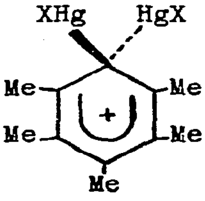
The oxidation of olefins to alcohols by aqueous mercuric sulfate proceeds by way of oxymercuration products (142).

B. AROMATIC COMPOUNDS

The interaction of mercuric trifluoroacetate in CF_3CO_2H with highly alkylated benzenes was investigated using nmr and uv spectroscopy (143). In most cases (durene, mesitylene, 7,12-dimethylbenzanthracene) crystalline mercuration products precipitated rapidly, but such solutions containing $Hg(O_2CCF_3)_2$ and C_6Me_6, C_6Et_6 or C_6Me_5H in CF_3CO_2H appeared to be stable. Unambiguous evidence for a $\left[C_6R_6\text{-}HgO_2CCF_3\right]^+$ π-complex could not be obtained via uv spectroscopy. Nmr spectra of solutions containing pentamethylbenzene suggested the presence of σ-complexes, $\boxed{49}$ and $\boxed{50}$, depending on



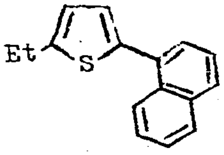
$\boxed{49}$



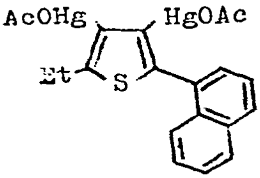
$\boxed{50}$

the amount of $Hg(O_2CCF_3)_2$ present. Dilution of such solutions with water resulted in precipitation of $C_6Me_5HgO_2CCF_3$.

The mercuration of $\boxed{51}$ gave $\boxed{52}$ (144) and other workers

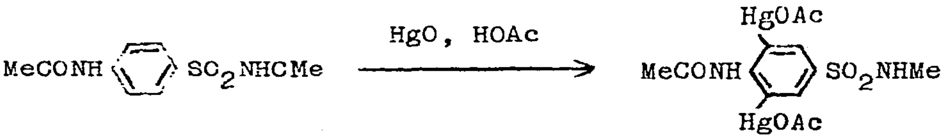


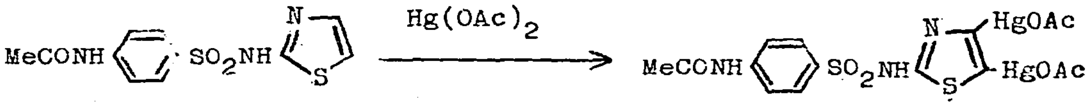
$\boxed{51}$



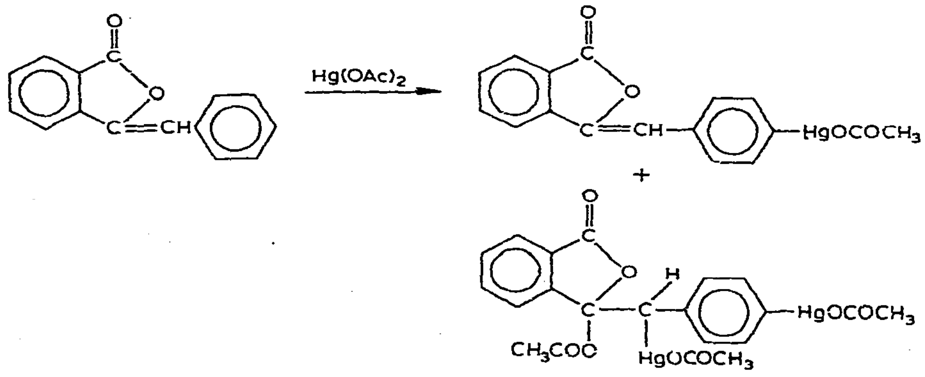
$\boxed{52}$

have mercurated various aromatic sulfonamides (145), e.g.:

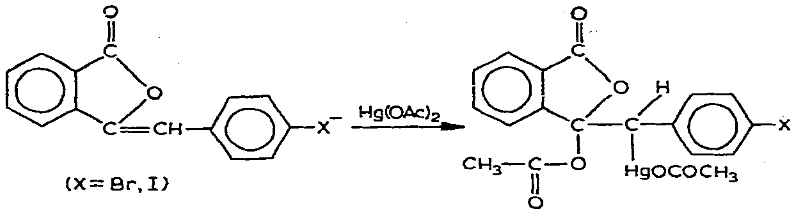


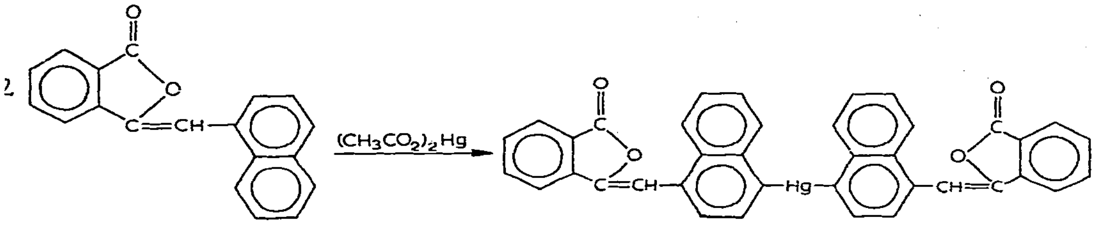


Czechoslovak workers have studied the action of mercuric acetate on various phthalides, obtaining either aromatic substitution or addition to olefinic C=C bonds (146):



$\boxed{53}$





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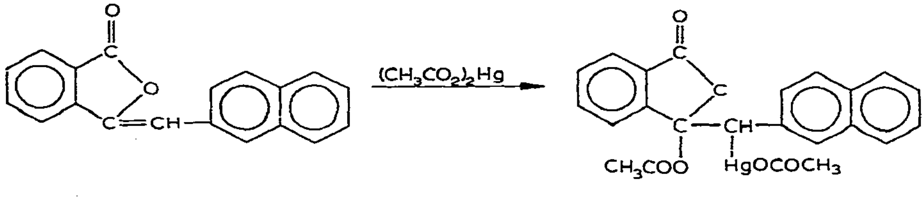
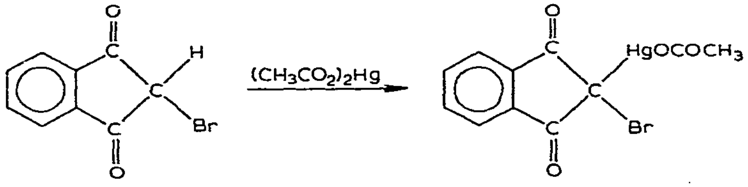
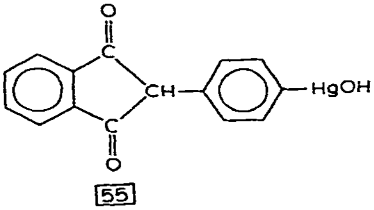
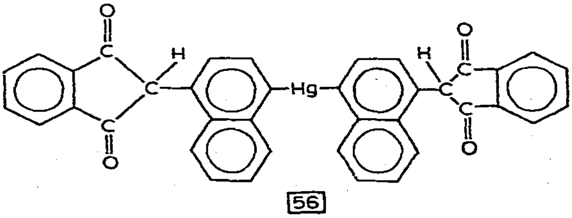




Also to be noted is the rearrangement of $\boxed{53}$ to $\boxed{55}$ and of $\boxed{54}$ to $\boxed{56}$ on treatment with catalytic quantities of NaOMe in methanol solution.



$\boxed{55}$



$\boxed{56}$

5. ORGANOFUNCTIONAL ORGANOMERCURY COMPOUNDS

Some references to organofunctional mercurials will be found in previous sections:

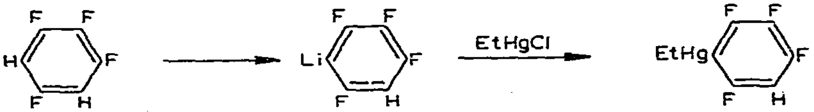
ferrocenyl-mercury compounds (12, 47)
cymantrenyl-mercury compounds (24)
polyfluoroarylmercurials (13, 14, 46)
polyfluoroalkylmercurials (22, 23)
vinylic mercurials (22, 23)
allylic mercurials (53)
alkynyl mercurials (63)
mercurials containing alkoxy (15), sulfur (16), ether (17), nitrogen (43), carbonyl (51, 62, 80) and cyano (66) functions.

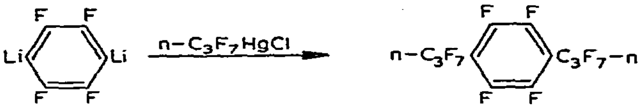
The solvomercuration of olefins (Section 4A) and the mercuration of substituted aromatics (Section 4B) give organofunctional organomercury products, and the halomethylmercurials (Section 3C) belong to the general class of organofunctional organomercury compounds.

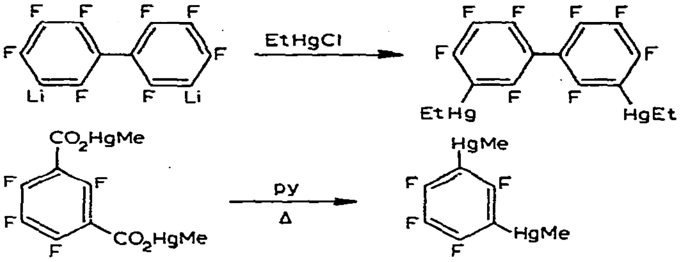
A. HIGHLY HALOGENATED ORGANOMERCURIALS

(See also Section 3C)

Mixed alkyl polyfluoroarylmercury compounds have been prepared (147):







The unsymmetrical mercurial $C_6F_5HgC_6Cl_5$ was prepared by the reaction (148):

$$C_6Cl_5HgCl + C_6F_5HgCH_3 \xrightarrow{\text{benzene, } 80^\circ} C_6F_5HgC_6Cl_5 + CH_3HgCl$$

The more obvious possible syntheses ($C_6F_5Li + C_6Cl_5HgCl$ and $C_6Cl_5Li + C_6F_5HgBr$) gave a mixture of $(C_6F_5)_2Hg$ and $(C_6Cl_5)_2Hg$ rather than the unsymmetrical product, due to the presence of LiCl which induces the symmetrization reaction. The action of anhydrous HCl on $C_6F_5HgC_6Cl_5$ resulted in exclusive cleavage of the C_6F_5 group. Complexes of $(C_6F_5)_2Hg$ have been reported (149):

$(C_6F_5)_2Hg{\cdot}L$ L = 4,4'-Me_2-2,2'-bipyridyl, 2,2'-biquinolyl, 2,2':6,2"-terpyridyl, 2,4,7,9-Me_4-1,10-phenanthroline, ethylenediamine, o-phenylenediamine, diphenylamine, pyridine, 4-cyanopyridine, triphenylphosphine and its oxide, 1,2-bisdiphenylarsinoethane

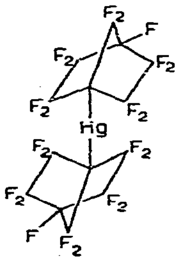
$(C_6F_5)_2{\cdot}2L$ L = di-2-pyridylamine

$\left[(C_6F_5)_2Hg\right]_2 L$ L = bisdiphenylphosphinomethane, bisdiphenylarsinomethane

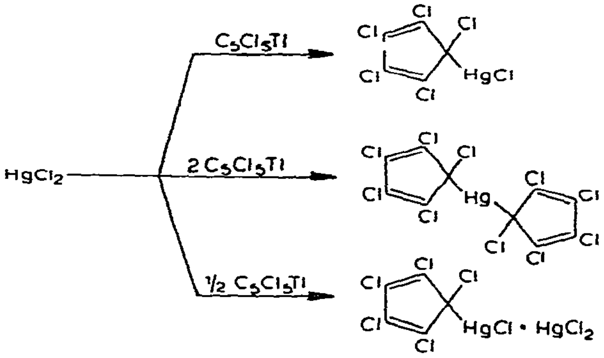
The structures of these complexes are discussed using experimental evidence derived from solution molecular weight measurements and uv and ir studies.

The direct reaction of 1-iodo-undecafluorobicyclo [2.2.1]-heptane with metallic mercury under uv irradiation gave [57] (150).

Stable, σ-bonded pentachlorocyclopentadienylmercury compounds have been prepared and their infrared and nuclear quadrupole resonance spectra were studied (151):



[57]



$$PhHgCl + C_5Cl_5Tl \longrightarrow PhHgC_5Cl_5$$

Knunyants and his coworkers have developed procedures for the synthesis of esters of α-mercurated fluorocarboxylic acids (152, 153):

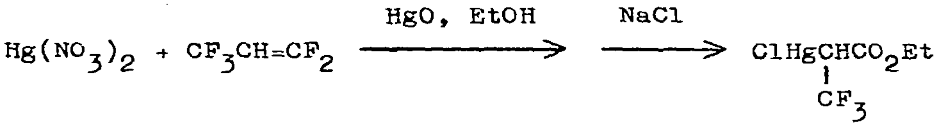
$$CF_2{=}CFOEt + HgX_2 \xrightarrow{EtOH} XHgCF_2CO_2Et + EtF + HX$$

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

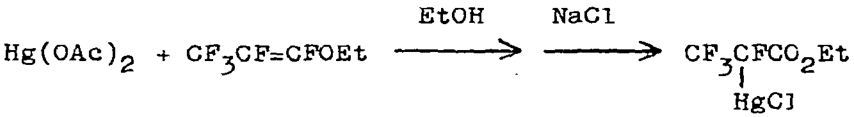
$$2\ PhHgNO_3 + 2\ CF_2{=}CFOEt \xrightarrow{EtOH} Ph_2Hg + Hg(CF_2CO_2Et)_2$$

$$+ 2\ EtF + 2\ HX$$

$$ClHgCF_2CO_2Et \xrightarrow[\text{room temp.}]{Cd/Hg} Hg(CF_2CO_2Et)_2$$



$$Hg(NO_3)_2 + CF_3CH{=}CF_2 \xrightarrow{HgO,\ EtOH} \xrightarrow{NaCl} ClHg\underset{\displaystyle CF_3}{\underset{|}{C}}HCO_2Et$$



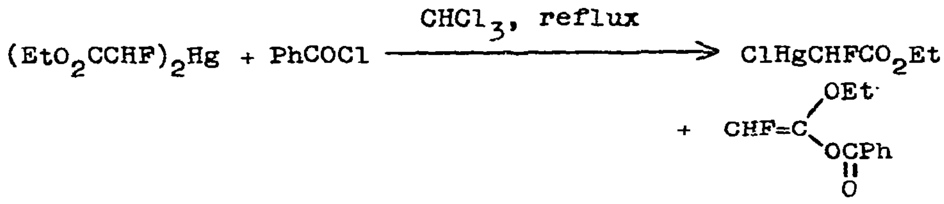
$$Hg(OAc)_2 + CF_3CF{=}CFOEt \xrightarrow{EtOH} \xrightarrow{NaCl} CF_3\underset{\displaystyle HgCl}{\underset{|}{C}}FCO_2Et$$

$$Hg(NO_3)_2 + (CF_3)_2C{=}CFOEt \xrightarrow{EtOH} \xrightarrow{NaCl} Hg\left[C(CO_2Et)(CF_3)_2\right]_2$$

$$Hg(OAc)_2 + CFCl{=}CFOEt \xrightarrow{EtOH} \xrightarrow{NaCl} ClHgCFClCO_2Et$$

$$Hg(OAc)_2 + CF_2{=}CFH \xrightarrow{EtOH} \xrightarrow{NaCl} ClHgCFHCO_2Et$$

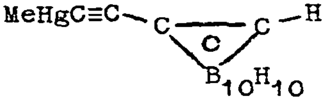
Hydrolysis of $AcOHgCF_2CO_2Et$ gave the insoluble, probably polmeric $\left[\overset{+}{Hg}CF_2CO_2^{-}\right]$, but $ClHgCF_2CO_2H$ could be prepared by reaction of the latter with the stoichiometric amount of HCl in ether (152). Aqueous and alcoholic HCl cleaved the C-Hg bond of such esters of α-mercurated fluorocarboxylic acids, but saponification with KOH in aqueous dioxane converted them to the potassium salts without C-Hg cleavage (154). Cleavage of C-Hg bonds in such esters also was effected with bromine and, in one example, benzoyl chloride (155):



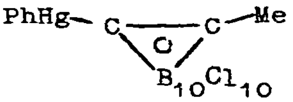
$$(EtO_2CCHF)_2Hg + PhCOCl \xrightarrow{CHCl_3,\ reflux} ClHgCHFCO_2Et + CHF{=}C(OEt)(OC(=O)Ph)$$

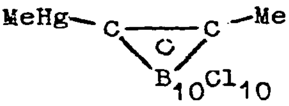
B. CARBORANYL-MERCURIALS

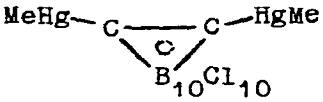
New organomercury derivatives of carboranes have been reported:

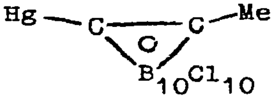


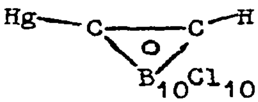
(prepared via the alkynyl lithium or copper(I) derivative (156))

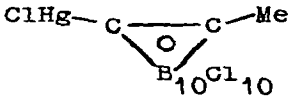




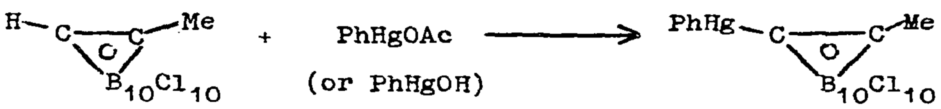


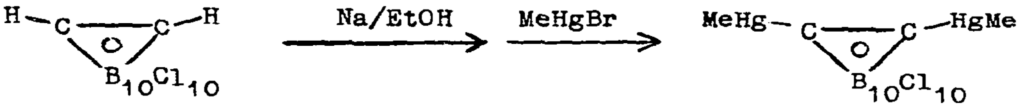






The mercury derivatives of the decachlorocarboranes were prepared by direct mercuration or via the anion (157):





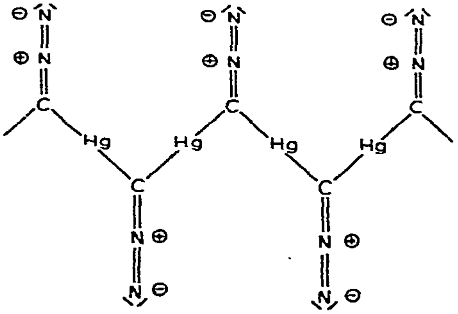
The C-Hg bonds in these compounds were readily cleaved by bromine.

C. MERCURATED DIAZOALKANES AND RELATED COMPOUNDS

New examples of mercurated aliphatic diazoalkanes, prepared by direct mercuration of the diazoalkane, have been described by several groups:
$Hg\left[C(N_2)P(O)(OMe)_2\right]_2$ (158), $Hg\left[C(N_2)P(O)Ph_2\right]_2$ and $Hg\left[C(N_2)P(O)(OEt)_2\right]_2$ (159), $RHgC(N_2)CO_2Et$ (R = Me, Et) and $(RHg)_2CN_2$ (R = Me, Et) (160). Mercury silylamide derivatives served well in the preparation of the latter (160):

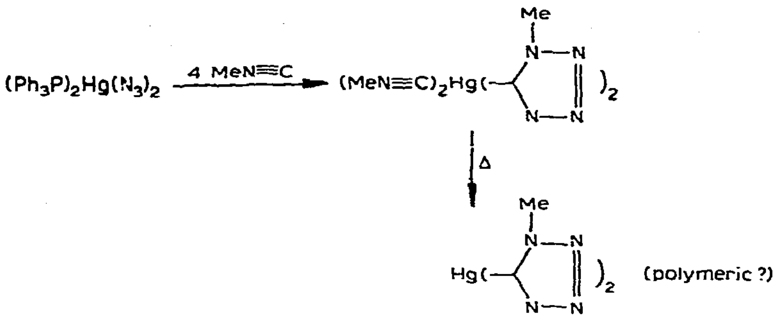
$$2\ RHgN(SiMe_3)_2 + CH_2N_2 \longrightarrow (RHg)_2CN_2 + 2\ HN(SiMe_3)_2$$

Treatment of diazomethane with $Hg\left[N(SiMe_3)_2\right]_2$ gave a polymeric, explosive solid believed to have the structure $\boxed{58}$ (160).

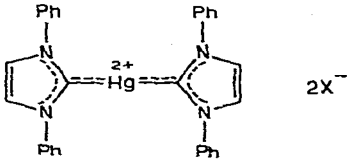


$\boxed{58}$

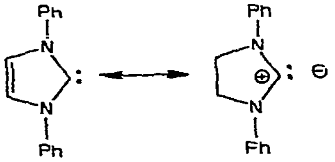
Also to be noted is the preparation of tetrazolato-mercury complexes (161):



Mercury compounds of type $\boxed{59}$ have been described previously by Wanzlick (OCR-B, 8 (1971) 489-490) and formulated as shown as complexes of Hg^{2+} with the nucleophilic carbene $\boxed{60}$. Such a formulation has been termed "bizarre" by Cooksey,

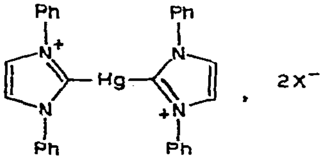


$\boxed{59}$



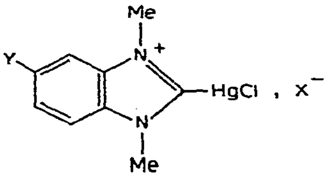
$\boxed{60}$

Dodd and Johnson (162), who suggested that the simple covalent structure $\boxed{61}$ is much more reasonable. These authors have



$\boxed{61}$

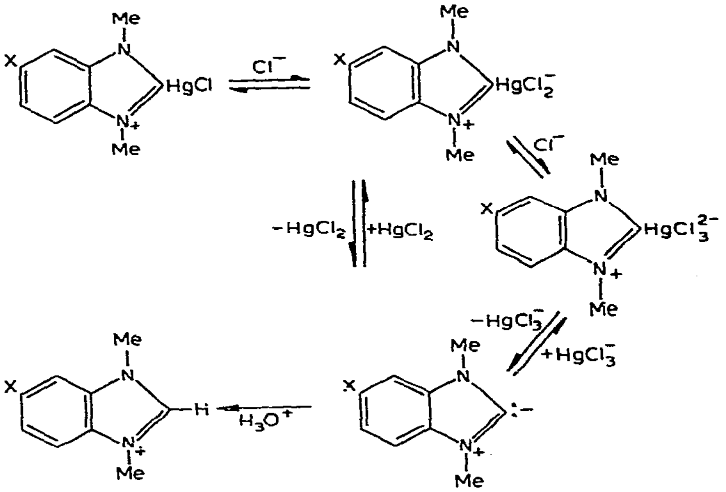
repared more members of this class of compounds, $\boxed{62}$.



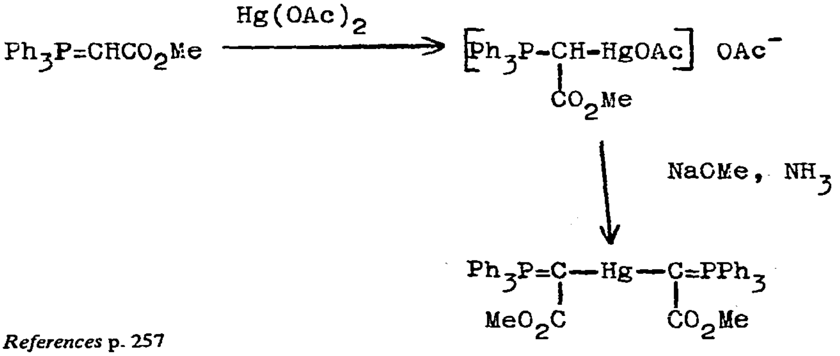
$\boxed{62}$

($Y = NO_2$, Cl, H, Me; $X = BF_4$, $HgCl_3$)

The rates of c-Hg cleavage of these mercurials by aqueous acid were measured and it was found that chloride ion catalyzed such reactions. The scheme shown below was suggested to be operative (162).

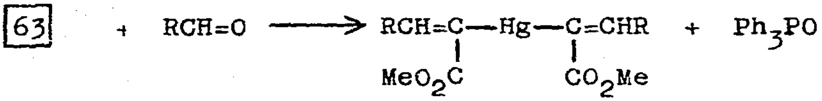


Mercurated phosphorus ylides serve nicely in the synthesis of vinylic mercurials (163):



$$Ph_3P{=}CHCO_2Me \xrightarrow{Hg(OAc)_2} \left[Ph_3P\text{-}\underset{CO_2Me}{CH}\text{-}HgOAc\right] OAc^- \xrightarrow{NaOMe,\ NH_3} Ph_3P{=}\underset{MeO_2C}{C}\text{—}Hg\text{—}\underset{CO_2Me}{C}{=}PPh_3$$

$\boxed{63}$

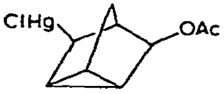


$$\boxed{63} + RCH{=}O \longrightarrow \underset{MeO_2C}{RCH{=}\overset{}{C}}{-}Hg{-}\underset{CO_2Me}{C}{=}CHR + Ph_3PO$$

Prepared in this manner were various $[ArCH{=}C(CO_2Me)]_2Hg$ (Ar = p- and m-$O_2NC_6H_4$, p-BrC_6H_4, Ph, p=$MeOC_6H_4$), $[MeCH{=}C(CO_2Me)]_2Hg$ and $[RCH{=}C(CN)]_2Hg$ (R = CCl_3 and p-$O_2NC_6H_4$) in yields ranging from 43-71%.

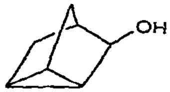
6. REACTIONS OF ORGANOMERCURIALS

The reduction of organomercurials of type RHgX by $NaBH_4$ and organotin hydrides was discussed in last year's Survey (OCR-B, 8 (1971) 492). Radical intermediates, RHg· and R·, were implicated by several lines of evidence. Jackson et al. (164, 165) have reported full details of their work in this area dealing mainly with stereochemical results of reductions of norbornenyl- and nortricyclylmercury compounds and with deuterium incorporation studies (cf. OCR-B, 8 (1971) 494). Reduction of $\boxed{64}$ by sodium naphthalenide (in excess) in THF gave and mixture of $\boxed{65}$ and $\boxed{66}$, i.e., essentially complete car-



$\boxed{64}$

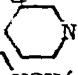
$\boxed{65}$

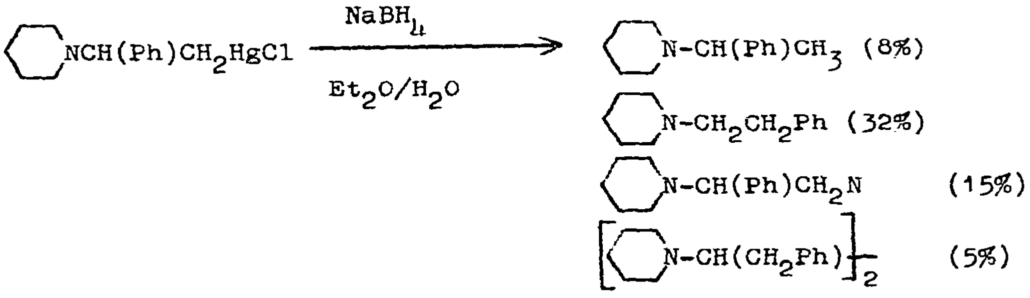


$\boxed{66}$

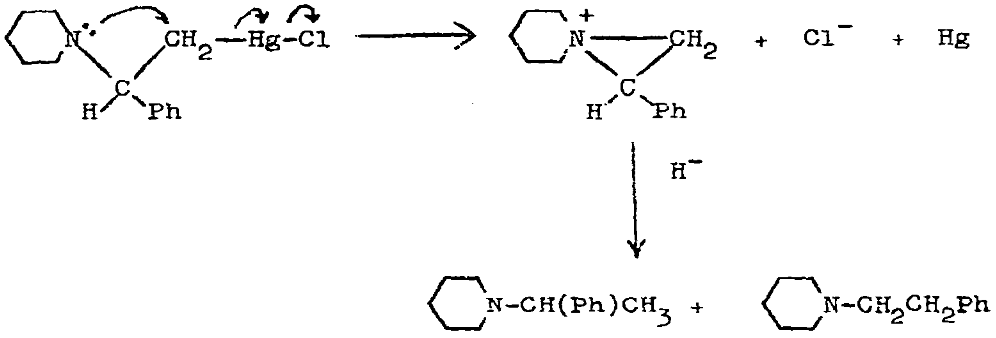
bon skeleton retention (166). Photolytic reduction of $\boxed{64}$ gave products in which the carbon skeleton retention was only 88%. Russian workers have studied $NaBH_4$ reduction of simple alkylmercuric chlorides and of PhHgCl, and on the basis of their results also suggest a radical mechanism ($RHgCl \longrightarrow RHgBH_4 \longrightarrow RHgH \longrightarrow RHg\cdot \longrightarrow R\cdot + Hg$) (167, 168).

Fluorinated mercurials of type $CF_3CH(HgCl)CH_2OR$ (R = alkyl or $COCH_3$) can be reduced with $NaBH_4$ to give $CF_3CH_2CH_2CR$ in 50-80% yield (169). The ethers (R = alkyl) are reduced to $CF_2{=}CHCH_2OR$ by zinc dust in aqueous NH_4Cl, but in the case of $CF_3CH(HgCl)CH_2C_2CCH_3$, deoxymercuration was the predominant reaction. Treatment of $CF_3CH(HgCl)CH_2OMe$ with $N_2H_4\cdot H_2O$ at 130° gave $CF_3CH_2CH_2OMe$ and $CF_2{=}CHCH_2OMe$ in low yield; at 100°, symmetrization to give $Hg(CH(CF_3)CH_2OMe)_2$ was the only observed process (169).

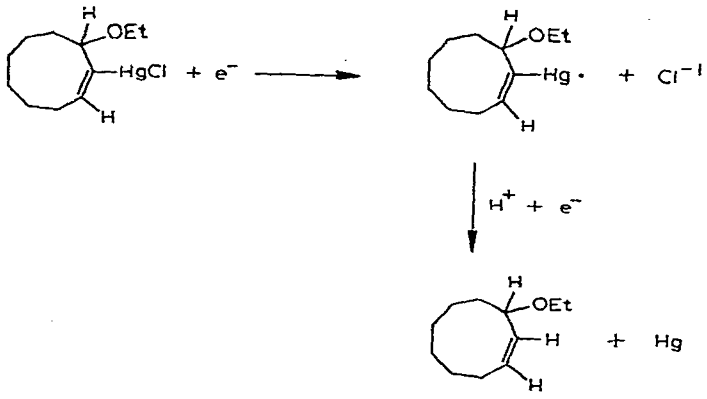
Aminomercuration products of various olefins have been demercurated with $NaBH_4$ and other reducing agents (170). Of the reagents tried in the case of  NCH_2CH_2HgCl (Na/Hg, $NaBH_4$, $LiAlH_4$, $LiBH_4$, N_2H_4), sodium borohydride gave the best yield of  NCH_2CH_3. Alkaline sodium borohydride reduced  $NCH(R)CH_2HgCl$ to  $NCH(R)CH_3$ (R = Ph, Me), but when aqueous-ethereal $NaBH_4$ was used, rearrangement and more complex products were obtained, e.g.:



Rearranged products also were obtained with Na/Hg, $LiAlH_4$ and alkaline hydrazine. The results were rationalized in terms of the operation of two mechanisms: (1) the usual radical mechanism alluded to above, and (2) an ionic mechanism proceeding via an intermediate aziridinium ion capable of rearrangement:



The polarographic reduction of 2-chloromercuri-3-ethoxycyclononene and 2-chloromercuri-3-ethoxycyclododecene in 50% dioxane-water was shown to go in two steps: first to the free radical RHg·, then to metallic mercury and the unsaturated ether (171):



The galvanostatic reduction of $(C_6F_5)_2Hg$ and C_6H_5HgBr at the mercury electrode has been studied (172).

The solvolysis of $CH_3CH_2{}^{14}CH_2HgClO_4$ in 10% dioxane-90% water, acetic or formic acids appeared to proceed via concurrent direct displacement and cationic processes as indicated by a small (0.6-3.5%) extent of isotopic scrambling to C-2 and C-3 (173). The isotopic scrambling process was discussed in terms of possible protonated cyclopropane intermediates. Oxidation of organomercuric halides and acetates by $Pb(OAc)_4$ in acetic acid at ca. 100° also appeared to generate carbonium ions (174). For instance, in the case of isobutylmercuric acetate, a mixture of iso-, sec-, and tert-butyl acetates (4.7:1: 1.8 ratio) was obtained, and in the case of n-propylmercuric chloride, a mixture of n-propyl and isopropyl acetates. It was suggested that the carbonium ions were formed from radical intermediates since some paraffinic and olefinic hydrocarbons also were formed. The anodic oxidation of organomercury compounds in aqueous acetonitrile gave products which suggested that the first step in the oxidation is C-Hg cleavage to give a carbonium ion (175). Thus when n-propylmercuric chloride was subjected to anodic oxidation at 2.2V in 0.1M $NaClO_4$ in 10:1 $MeCN:H_2O$, the products were $n\text{-}C_3H_7OH$ (28% current yield), $i\text{-}C_3H_7OH$ (11), $CH_3CONHC_3H_7\text{-}n$ (1) and $CH_3CONHC_3H_7\text{-}i$ (11). In the case of benzylmercuric chloride, the products under these conditions were $PhCH_2OH$ (7), PhCHO (60), $PhCO_2H$ (1), $CH_3CONH\text{-}CH_2Ph$ (16) and $PhCH_2CH_2Ph$ ($<$ 1).

The displacement of carbanions from suitable organomercurials (e.g., $PhHgCX_3$) by halide ions is a known reaction. Now Russian workers (176) have found that the action of catalytic quantities of fluoride ion on perfluoroalkylmercurials generates perfluoroalkyl carbanions which may be trapped, e.g.:

$$\left[(CF_3)_3C\right]_2Hg \xrightarrow[S_8]{KF/DMF} \left[(CF_3)_3CS\right]_2Hg$$

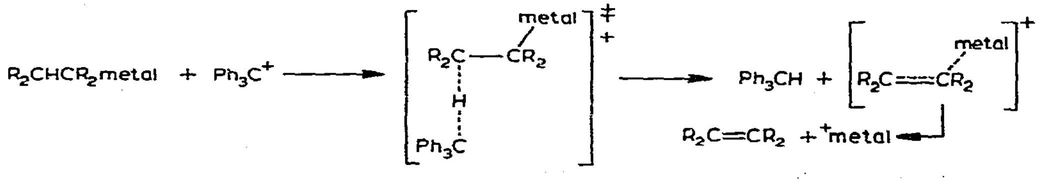
(no reaction in the absence of KF)

Potassium fluoride also catalyzed the redistribution of bis-perfluoroalkylmercurials with $HgCl_2$ and their cleavage by iodine in DMF. The action of sodium iodide on $[(CF_3)_2CR]_2Hg$ (R = F or CF_3) also resulted in perfluorocarbanion displacement, butvunder these conditions, fluoride ion loss to produce the olefins, $CF_2{=}C(R)CF_3$, occurred.

Reactions of trityl derivatives with organomercurials have been described previously by Reutov et al (OCR-B, 6 (1970) 292; 8 (1971) 496). The dehydromercuration of diisobutylmercury had been shown to proceed via β H^+ abstraction by $Ph_3C^+ClO_4^-$ via deuterium labelling and a concerted, cyclic mechanism had been postulated. In new work, Traylor and Jerkunica (177) demonstrated similar rapid dehydromercuration of Et_2Hg, $n\text{-}Bu_2Hg$ and $[PhCH_2CH(Me)]_2Hg$:

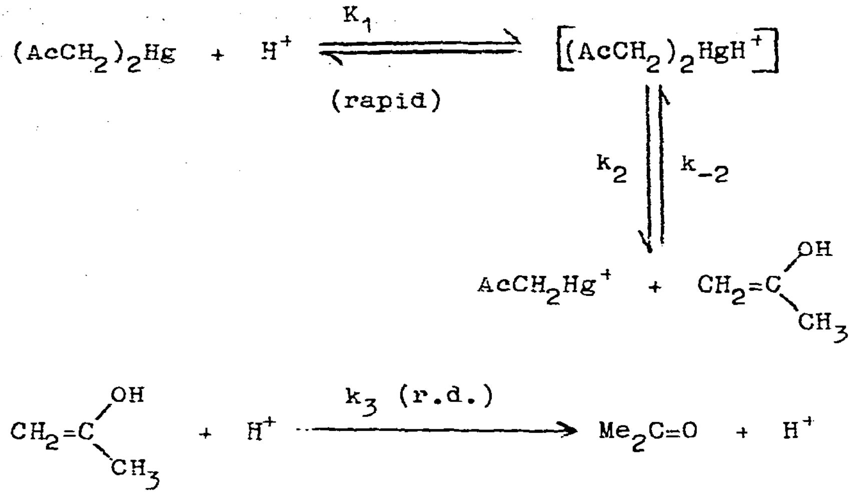
$$RCH_2CH_2HgCH_2CH_2R + Ph_3C^+BF_4^- \longrightarrow RCH_2CH_2HgBF_4 + Ph_3CH + RCH{=}CH_2$$

The compounds $(PhCMe_2CH_2)_2Hg$ and di-1-apocamphylmercury did not react with trityl fluoroborate, demonstrating the necessary presence of a β C-H bond and the importance of its geometry. The rate of such dehydromercurations was first order in mercurial and first order in trityl compound, and among the ethylmetal compounds examined, the rate per hydrogen decreased in the order $Et_4Pb > Et_2Hg > Et_4Sn > Et_4Ge > Et_4Si$. These reactions were pictured as going by way of vertical stabilized carbonium ions as shown:



Reutov and his coworkers have continued their work in this area. The action of trityl bromide on R_2Hg (R = Et, sec-Bu, i-Bu) resulted in predominant or total formation of Ph_3CH, but in addition to dehydromercuration, some coupling to give alkyltriphenylmetanes (Ph_3CEt, $Ph_3CCHMeEt$ and $Ph_3CCH_2CHMe_2$, respectively) also occurred (178). In reactions of $Ph_3C{\cdot}Br$ with diethyl- and di-sec-butylmercury the chemical and esr evidence indicated the formation of the trityl radical as an intermediate, i.e., an electron transfer process. The reaction of Ph_3C derivatives with diarylmercury compounds also gave indication of electron transfer reactions (179). The products formed in the presence of oxygen were a mixture of $Ph_3COOCPh_3$ and $ArCPh_3$ (60:40 in the case of diphenylmercury in 1,2-dichloroethane solution; 20:80 for $(p\text{-}ClC_6H_4)_2Hg$; 90:10 for $(p\text{-}MeO\text{-}C_6H_4)_2Hg$ in the same solvent). In the absence of oxygen, the $Ph_3C\cdot$ radical was detected by esr. The detection of chemically induced nuclear polarization in the nmr spectrum of Ph_3CCH_2Ph (from $Ph_3CBr + PhCH_2HgBr$) confirmed the operation of a radical process (180).

Protodemercuration rates of symmetrical mercurials, R_2Hg (R = $CF_2{=}CF$, $(CF_3)_2CH$, $(CF_3)_2CF$, C_6F_5, EtO_2CCF_2, CF_3, $PhSO_2CH_2$, $ClCH{=}CH$, $EtO_2C(Ph)CH$, $EtO_2C(CF_3)CH$, $PhC{\equiv}C$, and Ph) by HCl in DMF solution have been measured (181). A correlation between log k and the pK_a of the RH compound corresponding to the R_2Hg was sought (Fig. 1). The R_2Hg compounds in the left branch of the curve react by an $S_E1(N)$ mechanism (cf. ref. 9), those in the right branch by the S_E2 mechanism. The $HClO_4$-catalyzed cleavage of bis(acetylmethyl)mercury was shown to proceed by the following mechanism (182):



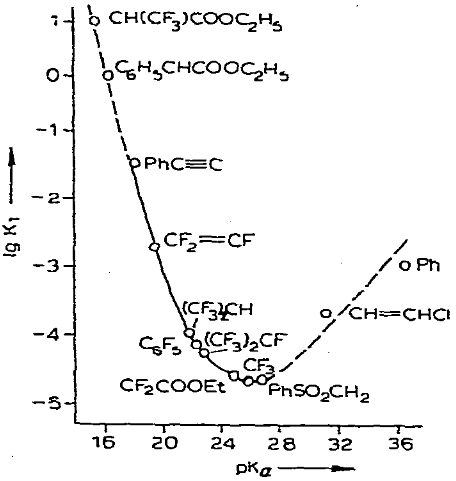
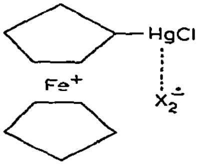


Fig. 1. Dependence of log k_1 for protodemercuration of R_2Hg on pK_a of RH in DMF. (181)

The protolysis kinetics of 1-methyl-1-acetyl-3-chloromercuri-indole have been studied (183, 184).

Detailed kinetic studies of the iododemercuration of R_2Hg (185) and RHgX (186, 187) compounds have been carried out by Reutov et al. When R was a strongly electron-attracting substituent (e.g., C_6F_5, $(CF_3)_3C$, etc.), an $S_E1(N)$ mechanism was indicated.

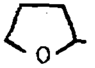
The formation of bromobenzene and iodobenzene in high yield by chlorinolysis of phenylmercuric bromide and iodide, respectively, has been the subject of a communication (188). In our opinion, this observation is by no means unexpected, oxidation of bromide and chloride ion, and of polar M-Br and M-I bonds by chlorine being known reactions. The Br_2 (or BrCl) and I_2 (or ICl) thus formed would lead to the observed products. The brominolysis and chlorinolysis of ferrocenylmercury compounds was shown to proceed via intermediate ferricenium species of type 67 when carried out at -20° in dichloromethane (189). Esr, Mössbauer and magnetic susceptibility measurements were cited.

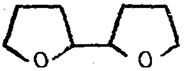


67

Other oxidation reactions of organomercurials have been studied. Oxidative degradation of di-n- and di-isopropylmercury by t-BuOOH and t-BuOOBu-t proceeded via intermediate $RHgOCMe_3$ species and gave as final products Hg, RHgOH, C_3H_8, C_3H_6, Me_3CO and PrOH (190). Oxidation of dibenzylmercury was found to be catalyzed by HCl in DMF, THF or dioxane at low mercurial concentrations (191). The intermediate peroxide, $PhCH_2OOHgCH_2Ph$, decomposed in the presence of NaCl to give $PhCH_2HgOH$ and benzaldehyde.

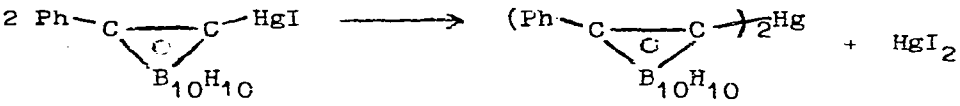
Photolysis of $Hg(CO_2Me)_2$ in THF gave the following products (192):

HCO_2CH_3 (50%),  CO_2CH_3 (21%), MeC_2C-CO_2Me (5.3%),

 (43%), Hg (100%)

It would seem that carbomethoxy radicals are generated in this photolysis. Diphenylmercury photolysis in THF gave quantitative yields of benzene, α,α'-bistetrahydrofuranyl and elemental mercury.

Substituent exchange reactions (symmetrization, disproportionation, redistribution) are important in organomercury chemistry. It is of interest that such reactions can occur in the solid phase at room temperature (193):



The colorless crystals of the iodomercuricarborane became red (due to HgI_2) on storage in the dark at 20° for several months. The occurrence of this reaction was attributed to strong I→Hg coordination in the dimeric molecules of the iodomercuricarborane. Much more facile were the solid phase reactions listed below (194).

$$Ph_2Hg + HgCl_2 \longrightarrow 2\ PhHgCl$$

$$Ph_2Hg + CCl_3HgCl \longrightarrow PhHgCCl_3 + PhHgCl$$

$$Ph_2Hg + Hg(CCl_3)_2 \longrightarrow 2\ PhHgCCl_3$$

$$HgCl_2 + PhHgCCl_3 \longrightarrow PhHgCl + CCl_3HgCl$$

The progress of these reactions was monitored by ir spectroscopy. All were complete within 4-10 hr. at 20°; the Ph_2Hg + $HgCl_2$ reaction was complete in 1 hr.

The symmetrization of arylmercuric halides to diarylmercurials can be accomplished by passing a chloroform solution of ArHgX through an alumina column which has been treated with NaCN (Table XV), a simple, practical procedure for small samples (195). In contrast, such treatment converts alkylmercuric halides to alkylmercuric cyanides rather than to dialkylmercurials. Stable anion radicals (naphthalenides or biphenylides) and solutions of alkali metals in $(Me_2N)_3PO$ also serve to symmetrize organomercuric halides, but the yields of R_2Hg are only 40-70% and some radical by-products derived from the mercurials are formed as well (196).

TABLE XV

SYMMETRIZATION OF ARYLMERCURY HALIDES (195)

Organomercury halide	Diarylmercury compound, R_2Hg % Yield
Ferrocenylmercury chloride	82, 91
1-Acetyl-2-chloromercuriferrocene	81, 86
Phenylmercury chloride	96, 89
1-Naphthylmercury chloride	90
2-Thienylmercury chloride	56
4-Phenoxyphenylmercury chloride	90
Phenylmercury cyanide	84

Nmr spectroscopy has been used to study organomercury substituent exchange reactions. In the system $(C_5H_5)_2Hg$/C_5H_5HgCl and in the pure components there is continuous, rapid intermolecular exchange of cyclopentadienyl and chlorine substituents at temperatures as low as -30° (197). The effectiveness of the solvent in promoting such exchange decreases in the order DMSO > DMF > py > ethers > $CDCl_3$ > CCl_4 > C_6H_6. Redistribution between $Hg(CH_2CHO)_2$ and diphenylmercury and p-substituted (MeO and Me_2N) diphenylmercurys was studied by ^1H nmr in DMSO and pyridine solution (198). Evidence for the unsymmetrical mercurials, $ArHgCH_2CHO$, was obtained. These findings have a bearing on the mechanism of radioisotopic exchange between pairs of symmetrical mercurials, R_2Hg and R'_2Hg suggesting that such exchange proceeds by way of unsymmetrical intermediates, RHgR'.

The isotopic exchange reaction between $(C_6F_5)_2Hg$ and $^{203}HgBr_2$ has been shown to be of the $S_E1(N)$ type, being catalyzed by bromide ion in benzene solution (199). In DMSO solution no added catalyst was needed since the solvent played the role of the nucleophilic catalyst. A critical (nonexperimental) study of isotopic exchange reactions of organomercurials which focussed on the consideration of three-dimensional potential energy surfaces and the principle of microscopic reversibility has been published (200).

7. MERCURY-FUNCTIONAL MERCURIALS

A useful preparation of methylmercuric fluoride has been described (201):

$$Me_2Hg + Hg_2F_2 \longrightarrow 2\ MeHgF + Hg$$

(The ir and Raman spectra of MeHgF are reported).

Anionic halide complexes of RHgCl (R = Me, Et) have been observed by spectrophotometry in acetonitrile solution (202). The halide source was trityl chloride:

$$Ph_3CCl + RHgCl \xrightarrow{MeCN} Ph_3C^+\ RHgCl_2^-$$

No such complexes were detected with n-propyl or phenylmercuric chlorides.

New organomercury pseudohalides have been reported:

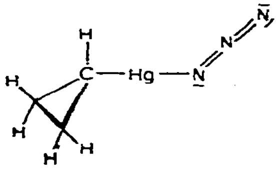
$$\mathrm{MeHgCl} + \mathrm{ClNCO} \longrightarrow \mathrm{MeHgNCO} + \mathrm{Cl_2} \qquad \text{(ref. 203)}$$

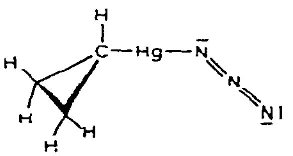
(The ir and Raman spectra of the volatile, vile-odored MeHgNCO are reported).

$$\mathrm{R_2Hg} + \mathrm{ClN_3} \longrightarrow \mathrm{RHgN_3} + \mathrm{RCl}$$

(R = cyclo-C_3H_5, cyclo-C_5H_9 and cyclo-C_6H_{11}) (ref. 204)

The vibrational spectra of these azides indicated the presence of cis-trans isomers, e.g.:





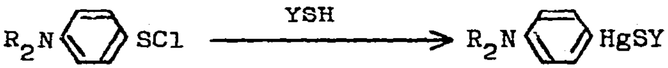
Organomercuric azides reacted with $(MeHg)_2O$ to give salts of the type $\left[(MeHg)_2OHgR'\right]N_3$ (R' = Me, Et, n-Pr, Ph) whose vibrational spectra were studied (205).

The hydrolytically sensitive peroxide $EtHgOOCMe_2Ph$, prepared by the reaction of EtHgCl with $PhMe_2COONa$, was found to be stable at room temperature for 1 month (206).

Organomercury thiophenoxides can be prepared via organogermanium, or better, organotin thiophenoxides (207):

$$\mathrm{R_3MSAr} + \mathrm{PhHgCl} \longrightarrow \mathrm{PhHgSAr} + \mathrm{R_3MCl} \qquad (\mathrm{M} = \mathrm{Ge, Sn})$$

Other organomercury sulfur compounds have been prepared (208):



(R = Me, Et; Y = $(EtO)_2P(S)$, $(BuO)_2P(S)$, C_9H_{19}, $Et_2NO(S)$, $HO_2CCH(NH_2)CH_2$)

The reaction of dithiophosphoric acid anhydrides with dialkylmercurials at 80-100° gave compounds of type $Hg(SP(S)RR')_2$ (209).

Degradation reactions of $(n\text{-}BuSe)_2Hg$ have been studied (210):

$$(BuSe)_2Hg \xrightarrow{160^\circ} Bu_2Se,\ Bu_2Se_2,\ HgSe,\ Hg$$

$$(BuSe)_2Hg \xrightarrow{UV} Bu_2Se,\ HgSe,\ Hg$$

The reaction of phenylmercuric chloride with polymeric di-n-butyltin oxide gave white, solid $PhHgOSnBu_2Cl$ (211).

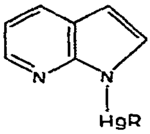
Several papers in 1971 were devoted to aminomercury compounds. The reaction of $MeHgN(SiMe_3)_2$ with liquid ammonia gave $(MeHg)_3N$, white needles with an unpleasant odor, in 30% yield (205). The vibrational, nmr and mass spectra are discussed. $MeHgN(SiMe_3)_2$ and $EtHgN(SiMe_3)_2$ were prepared via $LiN(SiMe_3)_2$ (212). The chemistry of these organomercury silylamides was investigated in some detail and they proved to be useful intermediates:

$$\begin{array}{lll} MeHgN(SiMe_3)_2 & + H_2O & \longrightarrow (MeHg)_2O \\ & + HN_3 & \longrightarrow MeHgN_3 \\ & + H_2NCN & \longrightarrow (MeHg)_2NCN \\ MeHgN(SiMe_3)_2 & + C_5H_6 & \longrightarrow MeHgC_5H_5 \end{array}$$

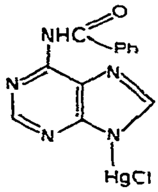
The reaction of $(Me_3Si)_2N\text{-}N(SiMe_3)Li$ with mercuric chloride gave $[(Me_3Si)_2N\text{-}N(SiMe_3)]_2Hg$ (213).

Reactions of n- and i-$PrHgOCMe_3$ with diethylamine were not clean, giving metallic mercury in substantial amount, as well as some C_3H_8 and C_3H_6 (214).

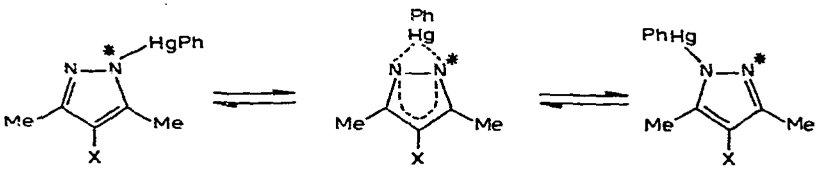
7-Azoindolatomercurials, $\boxed{68}$, have been prepared (215). Nmr studies suggested the nonchelated structure shown. Compounds of type $\boxed{69}$ gave found synthetic utility (216).


(R = Me, Ph)

$\boxed{68}$


$\boxed{69}$

A temperature-dependence nmr study of organomercury pyrazoles has demonstrated an intramolecular migration of the organomercury substituent (217). The rate of this exchange process decreased with decreasing temperature and at very low temperature (ca -100^o) a static system resulted.



($X = Cl, Br, NO_2$)

The bright yellow, explosive $Hg[N(Ph)NSO]_2$ has been prepared (218). Mercury bis-imidosulfuryldifluoride, $Hg(NSOF_2)_2$, has served as reagent for the synthesis of $Me_nSi(NSOF_2)_{4-n}$ ($n = 0-4$), $P(NSOF_2)_3$, $As(NSOF_2)_3$ and $OS(NSOF_2)_2$ (219).

Also to be noted are the reaction of $Hg(O_2SPh)_2$ with zinc dust to give $Zn(O_2SPh)_2$ and metallic mercury (220), the use of $Hg_2(O_2CCH{=}CH_2)_2$ in photosensitive plates (221), and two papers on organomercury dithizonates (222, 223).

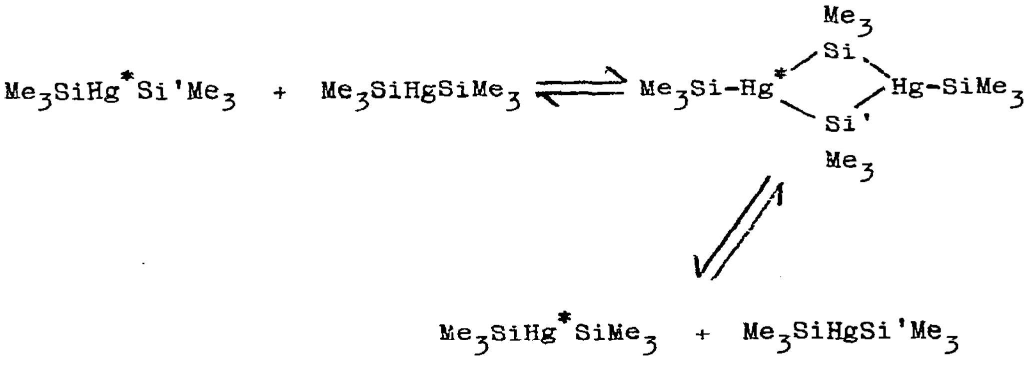
8. MERCURY-GROUP IV COMPOUNDS

A bis(trialkylstannyl)mercury compound which is quite stable has been prepared by Russian workers (224):

$$2\ (Me_3SiCH_2)_3SnH + Et_2Hg \longrightarrow \underset{\boxed{70}}{[(Me_3SiCH_2)_3Sn]_2Hg} + C_2H_6$$

$\boxed{70}$ does not decompose at its m.p.; pyrolysis at 150° gave $(Me_3SiCH_2)_4Sn$ and metallic mercury and tin. Oxidation produced $(Me_3SiCH_2)_3SnOSn(CH_2SiMe_3)_3$ and treatment with mercuric chloride gave $(Me_3SiCH_2)_3SnCl$ (via the unstable $(Me_3SiCH_2)_3SnHgCl$).

^1H nmr studies have shown $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ to undergo self-exchange in xylene and triethylamine via a second order process, presumably as shown below (225).



The analogous tin compound, $(Me_3Sn)_2Hg$, decomposed above -20°, but qualitative evidence for its self-exchange could be obtained. The rate of group exchange in the compounds investigated decreased in the order (R in R_2Hg): $Me_3Sn > Me_3Ge$

> Me_3Si > $MeCl_2Si$ > Me. The mixed compound $Me_3SiC{\equiv}CMe$ was shown to have rapid exchange of the propynyl group.

The substituent exchange reactions occurring between $(Me_3Si)_2Hg$ and other diorganomercurials have been investigated by nmr (226). Mixed species, Me_3SiHgR, were detected for R = Me, Ph, cyclo-C_3H_5, CH_2CHO, $CH_2{=}CH$, C_6Cl_5, $PhCH_2$ and $(Me_3Si)_2N$. Fairly rapid decomposition of these Me_3SiHgR compounds (to Me_3SiR) prevented determination of equilibrium constants. Russian workers have applied such reactions to preparative purposes (227, 228):

$$(Et_3Ge)_2Hg + HgR_2 \longrightarrow [Et_3GeHgR] \longrightarrow 2Et_3GeR + Hg$$

Thus prepared were $Et_3GeCH_2CO_2Me$, $Et_3GeC_6H_5$ and Et_3GeCN. When the ketones $Hg(CH_2COR)_2$ (R = Me and Et) were used, a mixture of Et_3GeCH_2COR and $Et_3GeC(R){=}CH_2$ resulted, in line with expectation (Lutsenko et al.). Similar reactions were observed with $(Et_3Si)_2Hg$.

Triphenylphosphine was found to be a catalyst for the oxidation of $(Et_3Si)_2Hg$ by molecular oxygen (229):

$$(Et_3Si)_2Hg + L \longrightarrow (Et_3Si)_2Hg{\cdot}L \qquad (L = Ph_3P)$$

$$(Et_3Si)_2Hg{\cdot}L + O_2 \longrightarrow Et_3SiHgOOSiEt_3 + L$$

$$Et_3SiHgOOSiEt_3 + (Et_3Si)_2Hg \longrightarrow 2\ Et_3SiHgOSiEt_3$$

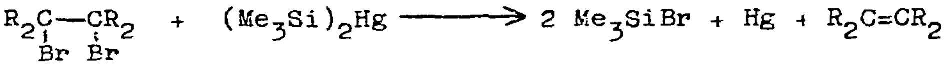
$$Et_3SiHgOSiEt_3 \longrightarrow Et_3SiOSiEt_3 + Hg \quad \text{(catalyzed by L)}$$

The autoxidation of $(Ph_3Ge)_2Hg$ in xylene at 15-50° has been studied (230). A molecular mechanism rather than a free radical process was indicated.

Esr studies have demonstrated one-electron transfer from $(Et_3Ge)_2Hg$ to tetracyanoethylene with precipitation of elemental mercury (231). The interaction of trityl chloride with $(Et_3Ge)_2Hg$ appears to be a radical process (232):

$$(Et_3Ge)_2Hg + 2\ Ph_3CCl \xrightarrow{20^\circ,\ PhMe} Hg + Et_3GeCl + \text{"}Ph_6C_2\text{"}$$

The mercurials $(Me_3Si)_2Hg$ and $(Me_3Ge)_2Hg$ dehalogenate vicinal dihalides (233):



$$\underset{Br}{R_2C}-\underset{Br}{CR_2} + (Me_3Si)_2Hg \longrightarrow 2\ Me_3SiBr + Hg + R_2C{=}CR_2$$

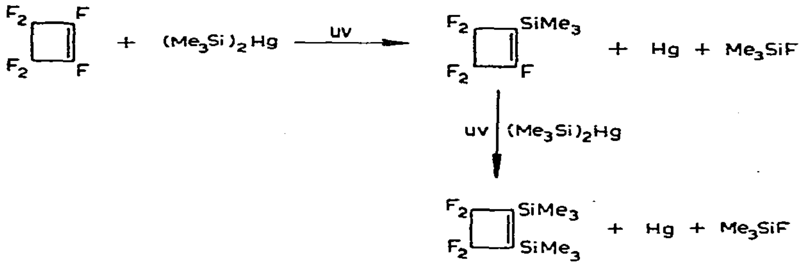
The debromination of erythro- and threo-2,3-dibromo-4-methylpentane was found to be stereospecifically cis, which speaks in favor of a molecular mechanism. 1,3-Dibromopropane was converted to cyclopropane by these mercurials. The reaction of $(Me_3Si)_2Hg$ with C_6F_5Br, which gives $Me_3SiC_6F_5$ as final product, has been shown to proceed via intermediate $C_6F_5HgSiMe_3$. Similar observations were made with $CF_2{=}CFBr$ (234):

$$CF_2{=}CFBr \xrightarrow[60^\circ\ \text{or uv}]{(Me_3Si)_2Hg} CF_2{=}CFHgSiMe_3 \xrightarrow{60^\circ\ \text{or uv}} \begin{array}{c} CF_2{=}CFSiMe_3 \\ + \\ Hg \end{array}$$

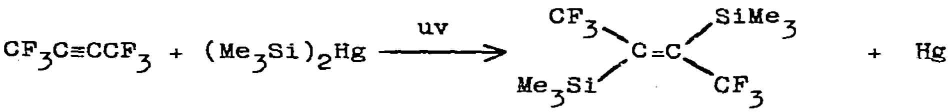
With other fluoroolefins, $(Me_3Si)_2Hg$ adds to the C=C bond in the first step (OCR-B, 8 (1971) 509). Full details of this work now have been provided (235). Some examples are:

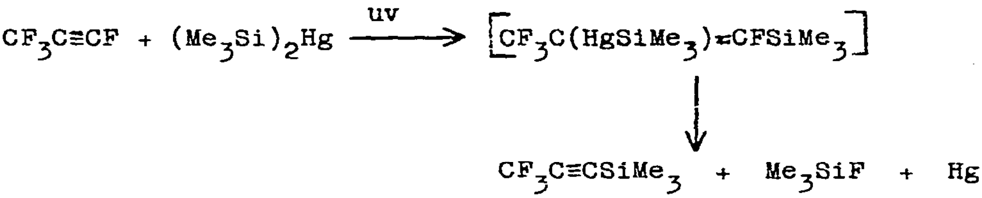
$$\begin{tikzcd} CF_2{=}CF_2 + (Me_3Si)_2Hg \arrow[r, "uv"] & Me_3SiHgCF_2CF_2SiMe_3 \arrow[d] \\ & CF_2{=}CFSiMe_3 + Hg + Me_3SiF \end{tikzcd}$$

(The similarity of this reaction to the double insertion of CCl_2 into $(Me_3Si)_2Hg$ (OCR-B, 8 (1971) 459) is to be noted).



Similar reactions occur with perfluoroacetylenes (235):

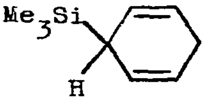




$$CF_3C\equiv CF + (Me_3Si)_2Hg \xrightarrow{uv} [CF_3C(HgSiMe_3)=CFSiMe_3] \longrightarrow CF_3C\equiv CSiMe_3 + Me_3SiF + Hg$$

The mechanism of these reactions was discussed and a radical process was favored.

Bis(trimethylsilyl)mercury reacts with aromatic hydrocarbons in the sense of homolytic substitution (236). For instance, reaction with benzene gave $PhSiMe_3$ and $\boxed{71}$, as well



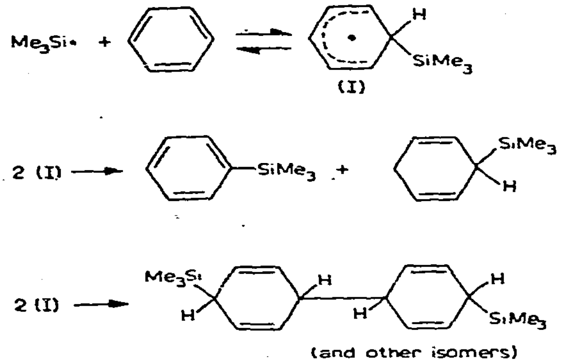
$\boxed{71}$

as small amounts of higher products. Hexamethyldisilane also was produced. The reaction course shown below was believed to be operative.

$$Hg(SiMe_3)_2 \xrightarrow{h\nu} Hg + 2\ Me_3Si\cdot$$

$$Me_3Si\cdot + Hg(SiMe_3)_2 \longrightarrow (Me_3Si)_2 + Hg + Me_3Si\cdot$$

$$2\ Me_3Si\cdot \longrightarrow (Me_3Si)_2$$



Bis(trimethylgermyl)mercury was less effective in this application. It was suggested that the photoexcited $(Me_3M^{IV})_2Hg^*$ molecules produce free $Me_3M^{IV}\cdot$ radicals only in the absence of reactive molecules with which the excited mercurial molecules could undergo a molecular reaction not involving radical intermediates. Among such "reactive" molecules are anisole and bromobenzene.

The synthesis of chalcogen-containing Group IV mercurials has been reported (237, 238):

$$(R_3M)_2Hg + 1/8\ Y_8 \longrightarrow R_3MYHgMR_3$$

$$(M = Si,\ Ge;\quad Y = S,\ Se;\quad R = Et,\ i\text{-}Pr)$$

$$(Et_3Ge)_2Hg + Et_3SiYH \longrightarrow Et_3GeH + Et_3GeHgYSiEt_3$$

$$(Y = S,\ Se,\ Te)$$

Mercury was eliminated in the slow room temperature decomposition or photolysis of these compounds, e.g.:

$$Et_3GeHgYSiEt_3 \longrightarrow Et_3GeYSiEt_3 + Hg \qquad (Y = S,\ Se,\ Te)$$

A reaction with metallic lithium also was recorded (238):

$$Et_3SiHgSSiEt_3 + 2\ Li \xrightarrow{\text{hexane}} Et_3SiLi + Et_3SiSLi + Hg$$

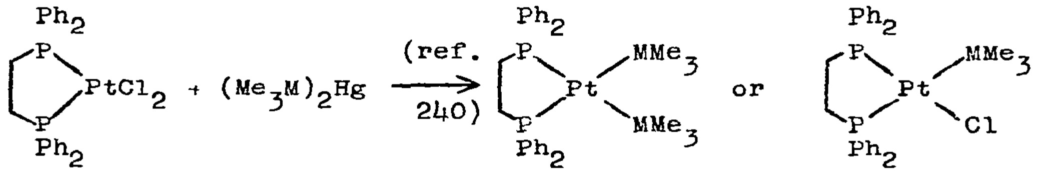
The use of $(i\text{-}Pr_3Ge)_2Hg$ in the synthesis of $i\text{-}Pr_3GeLi$ by reaction with metallic lithium has been reported (238).

Several examples of the use of Group IV-mercury compounds in the synthesis of Group IV-transition metal derivatives have been described:

$$(\pi\text{-}C_5H_5M^{VI}(CO)_3)_2Hg + (Et_3M^{IV})_2Hg \xrightarrow{\text{(ref. 239)}} 2\ Et_3M^{IV}\text{-}M^{VI}(CO)_3C_5H_5\text{-}\pi + Hg$$

$$\pi\text{-}C_5H_5M^{VI}(CO)_3HgCl + (Et_3M^{IV})_2Hg \xrightarrow{\text{(ref. 239)}} Et_3M^{IV}\text{-}M^{VI}(CO)_3C_5H_5\text{-}\pi + 2\ Hg + Et_3M^{IV}Cl$$

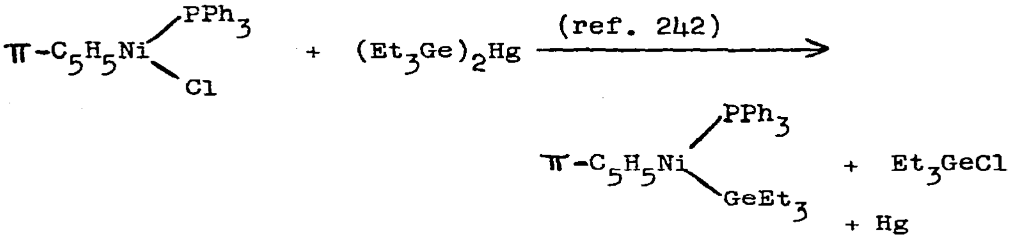
(M^{IV} = Si, Ge; M^{VI} = Cr, Mo, W)



$$trans\text{-}(Et_3P)_2Ir(CO)Cl + 2\ (Me_3M)_2Hg \xrightarrow{\text{(ref. 241)}} \underset{\boxed{72}}{(Et_3P)_2(CO)Ir(HgMMe_3)(MMe_3)_2} + Hg + Me_3MCl$$

(M = Si, Ge)

(Cleavage reactions of $\boxed{72}$ were examined. Treatment of the M = Ge compound with HCl gave $(Et_3P)_2(CO)Ir(HgCl)(GeMe_3)_2$ and its reaction with 1,2-dibromoethane gave $(Et_3P)_2(CO)Ir(HgBr)(GeMe_3)_2$.)



$$\pi\text{-}C_5H_5Ni(PPh_3)Cl + (Et_3Ge)_2Hg \xrightarrow{\text{(ref. 242)}} \pi\text{-}C_5H_5Ni(PPh_3)GeEt_3 + Et_3GeCl + Hg$$

The same product was obtained by reaction of nickelocene with $(Et_3Ge)_2Hg$ in the presence of triphenylphosphine (242).

Finally, we include some compounds containing Hg-P and Hg-B bonds in this section.

Salts of the $[(MeHg)_4P]^+$ cation have been prepared by reaction of PH_3 with MeHgX (X = BF_4, PF_6, SbF_6) (243). Vibration spectral, nmr and X-ray crystallographic data were provided.

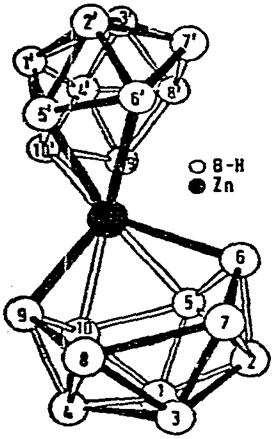


Fig. 2. Heavy atom structure of $[Zn(B_{10}H_{12})_2]^{2-}$; each boron is attached to one terminal hydrogen, and there are bridge hydrogens between the 6, 7 (6', 7') and 8, 9 (8', 9') positions (245).

Reaction of alkylmercuric halides, RHgY, with the decaborane-Grignard reagent, $B_{10}H_{13}MgX$, gave the solvated double salts of magnesium, $(MgY)_x\{Mg[Hg(B_{10}H_{10})_2]\}$ which dissolve in water to produce the ion $[Hg(B_{10}H_{10})_2]^{2-}$, a mercury(II) complex of the dodecahydro-nido-decaborate(2-) ion (244). An X-ray crystallographic study of the analogous $Zn(B_{10}H_{10})_2^{2-}$ salt showed the structure reproduced in Figure 2, and the Cd and Hg anions were found to be isostructural (245).

9. STRUCTURAL, SPECTROSCOPIC AND PHYSICAL STUDIES

A. STRUCTURAL STUDIES

An X-ray crystal structure of $[(C_6F_5)_2Hg]_2[Ph_2AsCH_2CH_2AsPh_2]$ showed three coordination for mercury in this molecule with approximately T-shaped stereochemistry (246). The structures of methyl- and phenyl-o-carboranylmercuric bromide and of phenyl-o-carboranylmercuric iodide have been determined by X-ray crystallography (193).

B. SPECTROSCOPIC STUDIES

i. Vibrational Spectra

The vibrational spectra of $(CH_3CH_2)_2Hg$ and $(CD_3CH_2)_2Hg$ (247), the vinylmercuric halides (248), divinylmercury (249), σ-indenylmercurials (250), the methylmercuric halides (X = Cl, Br, I) in the vapor phase (251), $(MeHg)_3N$ and $(MeHg)_2O$ (205), and MeHg-ammonium salts ($H_nN(HgMe)_{4-n}{}^+ClO_4{}^-$ and the N-D analogs, where n = 0-3) (252) have been measured and discussed, as have been the rotation-vibration spectra of $(CH_3)_2Hg$ and $(CD_3)_2Hg$ (253). The valence force field for $(CH_3)_2Hg$ has been determined (254).

ii. Nuclear Magnetic Resonance Studies

To be noted are nmr studies of some arylmercury compounds (PhHgCl, various isomeric mono-, di-, tri- and tetramethylphenylmercuric halides, various p- and m-RC_6H_4HgCl, where R = F, Cl, Br, CF_3 and OMe) (255), of various $RHgCH_3$ compounds (J_{Hg-C-H} for R = Me, PhC≡C and 14 carborane derivatives in 10 different solvents) (256), of $(CF_2{=}CF)_2Hg$ and $MeHgCF{=}CF_2$ (^{19}F and ^{199}Hg nmr) (257), of di-2-furyl- and di-2-thienylmercury (258), of the fluxional, σ-bonded $(MeC_5H_4)_2Hg$ (temperature dependence) (259), and of isomeric $CF_3C_6H_4Hg$ compounds (260). Evidence was presented in the latter study for through-space coupling between Hg and F in o-$CF_3C_6H_4HgX$ compounds.

iii. Mass Spectrometry

The mass spectral fragmentation of diaryl- and dialkylmercurials and of functional derivatives ($ClHgCH_2COCH_3$, $ClHgCH_2CHO$, etc.) was studied in detail and discussed (261). When pairs of symmetrical mercurials, R_2Hg and R'_2Hg, were introduced into the mass spectrometer, ions of type $[RHgR']^{+\cdot}$ were observed in addition to $[R_2Hg]^{+\cdot}$ and $[R'_2Hg]^{+\cdot}$ (261). Also examined was the fragmentation under electron impact of $Me_2C{=}C(HgCl)_2$ and $CH_3CH(HgCl)_2$ (262), C_6Cl_5 and $CCl_2{=}CCl$ mercury compounds (263) and trihalomethylmercury compounds (71, 72).

Vapor phase bimolecular reactions of R_2Hg^+, RHg^+ and Hg^+ with neutral molecules have been observed in the mass spectrometer (264).

C. OTHER PHYSICAL STUDIES

The dissociation energy of the first C-Hg bond in diethylmercury, D(EtHg-Et) has been determined to be 43.7 kcal/

mole by the toluene carrier pyrolysis method (265). D(Hg-Et) thus is 6.5 kcal/mole.

10. MISCELLANEOUS

Among miscellaneous items to be noted are the use of dimethylmercury as an enhancer of spin-forbidden transitions (266) and of p-$R_2NC_6H_4HgOAc$ (R = Me, Et) compounds in the extraction-photometric determination of sulfhydryl groups (267).

The analysis of Hg^{2+} in the presence of organomercurials has received attention (268-270). Separation of traces of Hg^{2+} from organomercurials in aqueous solution could be accomplished by adsorption on microbeads of soda lime (271). Methylmercury and inorganic mercury collection by a selective chelating resin has been reported (272).

Precautions to be used in handling methylmercurials have been suggested (273), and this article elicited a remarkable reply from G. F. Wright, an organomercury chemist of long standing (274).

A biochemical model for the biological methylation of mercury has been suggested from results of methylation studies in vivo with Neurospora crassa (275). The subject of mercury (including methylmercury) in the environment has been reviewed (276).

11. REFERENCES

1. L. G. Makarova, Organometal. Reactions, 2 (1971) 335
2. N. S. Vyazankin, G. A. Razuvaev and O. A. Kruglaya, Z. Chem., 11 (1971) 53

3. N. S. Vyazankin, G. A. Razuvaev and O. A. Kruglaya, Organometal. Chem. Synth., 1 (1971) 205

4. D. Seyferth, Pure Appl. Chem., 23 (1971) 391

5. S. F. Zhil'tsov and O. N. Druzhkov, Usp. Khim., 40 (1971) 226; Russ. Chem. Rev., 40 (1971) 126

6. D. Seyferth and R. J. Spohn, Trans. New York Acad. Sci., Ser. II, 33 (1971) 625

7. G. Chandra, M. S. Muthana and D. Devaprabhakara, J. Sci. Ind. Res., 30 (1971) 333

8. H. Arzoumanian and J. Metzger, Synth. (1971) 527

9. I. P. Beletskaya, K. P. Butin and O. A. Reutov, Organometal. Chem. Rev. A , 7 (1971) 51

10. L. Fishbein, Chromatog. Rev., 13 (1970) 83

11. L. Dunlap, Chem. Eng. News, 49 (1971) 22 (July 5 issue)

12. D. W. Slocum, C. A. Jennings, T. R. Engelmann, B. W. Rockett and C. R. Hauser, J. Org. Chem., 36 (1971) 377

13. S. C. Cohen, Jr., S. H. Sage, W. A. Baker, Jr., J. M. Burlitch and R. B. Petersen, J. Organometal. Chem., 27 (1971) C44

14. T. A. George, J. Organometal. Chem., 33 (1971) C13

15. H. H. Grootveld, C. Blomberg and F. Bickelhaupt, Tetrahedron Lett. (1971) 1999

16. M. T. Rahman, M. R. Smith, Jr., A. F. Webb and H. Gilman, Organometal. Chem. Synth., 1 (1971) 105

17. K. G. Taylor, W. E. Hobbs and M. Sacquet, J. Org. Chem., 36 (1971) 369

18. B. L. Dyatkin, S. R. Sterlin, B. I. Martynov, E. I. Mysov, and I. L. Knunyants, Tetrahedron, 27 (1971) 2843

19. R. C. Larock and H. C. Brown, J. Organometal. Chem., 26 (1971) 35

20. K. Issleib, S. Naumann, H. Matschiner and B. Walther, Z. anorgan. allgem. Chem., 381 (1971) 226

21. D. Datta, B. Majee and A. K. Ghosh, J. Organometal. Chem., 29 (1971) 251

22. S. Patai, D. Elmaleh and Z. Rappoport, J. Chem. Soc. C (1971) 3100

23. A. N. Nesmeyanov, T. P. Tolstaya, N. F. Sokolova, V. N. Varfolomeeva and A. N. Petrakov, Dokl. Akad. Nauk SSSR, 198 (1971) 115

24. A. N. Nesmeyanov, V. A. Sazonova and N. N. Sedova, Dokl. Akad. Nauk SSSR, 198 (1971) 590

25. E. G. Perevalova, T. V. Baukova, E. I. Goryunov and K. I. Grandberg, Izv. Akad. Nauk SSSR, Ser. Khim. (1970) 2148

26. G. N. Schrauzer, J. H. Weber, T. M. Beckham and R. K. Y. Ho, Tetrahedron Lett. (1971) 275

27. J.-Y. Kim, N. Imura, T. Ukita and T. Kwan, Bull. Chem. Soc. Japan, 44 (1971) 300

28. N. Imura, E. Sukegawa, S.-K. Pan, K. Nagao, J.-Y. Kim, T. Kwan and T. Ukita, Science, 172 (1971) 1248

29. A. Adin and J. H. Espenson, Chem. Comm. (1971) 653

30. A. A. Koksharova, G. G. Petukhov and S. F. Zhil'tsov, Zh. Obshch. Khim., 40 (1970) 2446

31. S. F. Zhil'tsov, A. A. Koksharova and G. G. Petukhov, Zh. Obshch. Khim., 41 (1971) 1060

32. G. M. Whitesides and D. J. Boschetto, J. Amer. Chem. Soc., 93 (1971) 1529

33. E. Vedejes and M. F. Salomon, Chem. Comm. (1971) 1582

34. R. A. G. Marshall and D. R. Pollard, J. Organometal. Chem., 27 (1971) 149

35. V. R. Polishchuk, L. S. German and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 620

36. Yu. A. Ol'dekop, N. A. Maier and Yu. D. Butko, Zh. Obshch. Khim., 41 (1971) 2253

37. Yu. A. Ol'dekop, N. A. Maier, Yu. D. Butko and M. S. Mindel, Zh. Obshch. Khim., 41 (1971) 828

38. Yu. A. Ol'dekop, N. A. Maier, Yu. D. Butko and M. S. Mindel Zh. Obshch. Khim., 41 (1971) 1066

39. Yu. A. Ol'dekop, N. A. Maier and Yu. A. Dzhomidava, Vesti Akad.Navuk Belarus. SSR, Ser. Khim. Navuk (1971) 115; Chem. Abstr., 75 (1971) 36280d

40. Yu. A. Ol'dekop, N. A. Maier and A. A. Erdman, Vesti Akad. Navuk Belarus. SSR, Ser. Kihim. Navuk (1971) 74; Chem. Abstr., 74 (1971) 124585s

41. P. G. Cookson and G. B. Deacon, J. Organometal. Chem., 27 (1971) C9; P. G. Cookson and G. B. Deacon, Austral. J. Chem., 24 (1971) 150

42. J. Yamamoto and C. A. Wilkie, Inorg. Chem., 10 (1971) 1129

43. G. Fraenkel and J. W. Cooper, J. Amer. Chem. Soc., 93 (1971) 7228

44. J. J. Eisch and J.-M. Biedermann, J. Organometal. Chem., 30 (1971) 167

45. K. Margolis and K. Dehnicke, J. Organometal. Chem., 33 (1971) 147

46. G. B. Deacon and J. C. Parrott, Inorg. Nucl. Chem. Lett., 7 (1971) 329; Austral. J. Chem., 24 (1971) 1771

47. G. Marr and T. M. White, J. Organometal. Chem., 30 (1971) 97

48. B. L. Dyatkin, B. I. Martynov, I. L. Knunyants, S. R.

Sterlin, L. A. Fedorov and Z. A. Stumbrevichute, Tetrahedron Lett. (1971) 1345

49. B. Gassenheimer and T. Wartik, Inorg. Chem., 10 (1971) 650
50. V. A. Chauzov and Yu. I. Baukov, Zh. Obshch. Khim., 40 (1970) 1426
51. Z. S. Novikova, N. P. Galitskova, V. A. Kozlov and I. F. Lutsenko, Zh. Obshch. Khim., 41 (1971) 831
52. Y. Okamoto and T. Yano, J. Organometal. Chem., 29 (1971) 99
53. A. N. Nesmeyanov, A. Z. Rubezhov, S. P. Gubin, A. S. Ivanov and L. I. Voronchikhina, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 2359
54. B. Crociani, M. Nicolini and T. Boschi, J. Organometal. Chem., 33 (1971) C81
55. D. Seyferth, R. J. Spohn and J. E. Hallgren, J. Organometal. Chem., 28 (1971) C34
56. S. W. Breuer, M. J. Leatham and F. G. Thorpe, Chem. Comm. (1971) 1475
57. R. F. Heck, J. Amer. Chem. Soc., 93 (1971) 6896
58. R. F. Heck, J. Organometal. Chem., 33 (1971) 399
59. R. J. Ouellette and C. Levin, J. Amer. Chem. Soc., 93 (1971) 471
60. G. T. Rodeheaver and D. F. Hunt, Chem. Comm. (1971) 818
61. Y. Hirota, M. Ryang and S. Tsutsumi, Tetrahedron Lett. (1971) 1531
62. M. A. Kazankova, L. I. Petrovskaya and I. F. Lutsenko, Zh. Org. Khim., 7 (1971) 58
63. W. Ried, W. Merkel and H. Knorr, Organometal. Chem. Synth., 1 (1971) 257
64. K. C. Bass and G. M. Taylor, J. Chem. Soc. C (1971) 1

65. K. C. Bass and P. Nababsing, Org. Prep. Proced. Int., 3 (1971) 45

66. G. Ahlgren, B. Akermark and M. Nilsson, J. Organometal. Chem., 30 (1971) 303

67. W. Kirmse, "Carbene Chemistry", 2nd edition, Academic Press, New York, 1971

68. A. K. Mal'tsev, R. G. Mikaelyan and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 199

69. O. M. Nefedov, A. K. Mal'tsev and R. G. Mikaelyan, Tetrahedron Lett. (1971) 4125

70. A. K. Mal'tsev, R. G. Mikaelyan, O. M. Nefedov, R. H. Hauge and J. L. Margrave, Proc. Nat. Akad. Sci. U.S., 68 (1971) 3238

71. A. K. Mal'tsev, O. M. Nefedov, R. H. Hauge, J. L. Margrave and D. Seyferth, J. Phys. Chem., 75 (1971) 3984

72. A. K. Mal'tsev, R. G. Mikaelyan and O. M. Nefedov, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 1179

73. D. Seyferth and C. K. Haas, J. Organometal. Chem., 30 (1971) C38

74. D. Seyferth, C. K. Haas and S. P. Hopper, J. Organometal. Chem., 33 (1971) C1

75. V. I. Shcherbakov, Zh. Obshch. Khim., 41 (1971) 1095

76. D. Seyferth and H. Shih, Organometal. Chem. Synth., in press

77. D. Seyferth and D. C. Mueller, J. Amer. Chem. Soc., 93 (1971) 3714

78. D. Seyferth and D. C. Mueller, J. Organometal. Chem., 28 (1971) 325

79. D. Seyferth and E. M. Hanson, J. Organometal. Chem., 27 (1971) 19

80. H. O. House, W. F. Fisher, Jr., M. Gall, T. E. McLaughlin and N. P. Peet, J. Org. Chem., 36 (1971) 3429

81. D. Seyferth and S. P. Hopper, J. Organometal. Chem., 26 (1971) C62

82. D. Seyferth and S. B. Andrews, J. Organometal. Chem., 30 (1971) 151

83. V. I. Shcherbakov and S. F. Zhil'tsov, Zh. Obshch. Khim., 40 (1970) 2046

84. B. I. Rabosin, S. F. Zhil'tsov and G. G. Petukhov, Izv. Vyssch. Ucheb. Zaved., Khim. Khim. Tekhnol., 14 (1971) 1047; Chem. Abstr., 75 (1971) 151173h

85. P. J. Van Vuuren, R. J. Fletterick, J. Meinwald and R. E. Hughes, J. Amer. Chem. Soc., 93 (1971) 4394

86. E. Rosenberg and J. J. Zuckerman, J. Organometal. Chem., 33 (1971) 321

87. M.-C. Sacquet, B. Graffe and P. Maitte, Bull. Soc. Chim. France (1971) 2557

88. S. D. Saraf, Synth. (1971) 264

89. P. Svoboda and V. Chvalovský, Coll. Czech. Chem. Commun. 36 (1971) 2174

90. D. Seyferth, H. D. Simmons, Jr. and H. M. Shih, J. Organometal. Chem., 29 (1971) 359

91. W. H. de Wolf, W. Stol, I. L. Landheer and F. Bickelhaupt, Rec. trav. chim., 90 (1971) 405

92. L. Spialter, W. A. Swansiger, L. Pazdernik and M. E. Freeburger, J. Organometal. Chem., 27 (1971) C25

93. D. Seyferth, H. Shih, P. Mazerolles, M. Lesbre and M. Joanny, J. Organometal. Chem., 29 (1971) 371

94. D. Seyferth and Y. M. Cheng, J. Amer. Chem. Soc., 93 (1971) 4072

95. D. Seyferth, R. Damrauer, S. B. Andrews and S. S. Washburne, J. Amer. Chem. Soc., 93 (1971) 3709

96. D. Seyferth and W. E. Smith, J. Organometal. Chem., 26 (1971) C55

97. C. W. Martin and J. A. Landgrebe, Chem. Commun. (1971) 15

98. C. W. Martin, J. A. Landgrebe and E. Rapp, Chem. Commun. (1971) 1438

99. H. H. Gibson, Jr., J. R. Cast, J. Henderson, C. W. Jones, B. F. Cook and J. B. Hunt, Tetrahedron Lett. (1971) 1825

100. D. Seyferth, R. Damrauer, H. Shih, W. Tronich, W. E. Smith and J. Y.-P. Mui, J. Org. Chem., 36 (1971) 1786

101. H. G. Braxton, Jr. and E. J. Lajiness, U.S. patent 3,501,283 (1970) (to Ethyl Corporation)

102. G. Olah and P. R. Clifford, J. Amer. Chem. Soc., 93 (1971) 1261

103. G. A. Olah and P. R. Clifford, J. Amer. Chem. Soc., 93 (1971) 2320

104. R. D. Bach and R. F. Richter, Tetrahedron Lett. (1971) 3915

105. H. C. Brown and K.-T. Liu, J. Amer. Chem. Soc., 93 (1971) 7335

106. V. I. Sokolov, Dokl. Akad. Nauk SSSR, 197 (1971) 362

107. D. J. Pasto and J. A. Gontarz, J. Amer. Chem. Soc., 93 (1971) 6902

108. D. J. Pasto and J. A. Gontarz, J. Amer. Chem. Soc., 93 (1971) 6909

109. D. Jasserand, R. Granger, J.-P. Girard and J.-P. Chapat, Compt. rend. **Acad. Sci., Paris, C,** 272 (1971) 1693

110. V. I. Sokolov, L. I. Troitskaya and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1970) 2648

111. R. M. Carlson and A. H. Funk, Tetrahedron Lett. (1971) 3661

112. P. Seidl, M. Robetts and S. Winstein, J. Amer. Chem. Soc., 93 (1971) 4089

113. H. J. Franz, W. Höbold, R. Höhn, G. Müller-Hagen, R. Müller, W. Pritzkow and H. Schmidt, J. prakt. Chem., 312 (1970) 622

114. J. E. Byrd, L. Cassar, P. E. Eaton and J. Halpern, Chem. Commun. (1971) 40

115. D. Kühnle and W. Funke, Angew. Chem., 83 (1971) 369

116. H. Christol, F. Plénat and J. Revel, Bull. Soc. Chim. France (1971) 4537

117. J. Perie, J. P. Laval and A. Lattes, Compt. rend. Acad. Sci., Paris, C, 272 (1971) 1141

118. J. Perie, J. P. Laval, J. Roussel and A. Lattes, Tetrahedron Lett. (1971) 4399

119. J. L. Jernow, D. Gray and W. D. Closson, J. Org. Chem., 36 (1971) 3511

120. M. Kocór and M. Gumulka, Rocz. Chem., 45 (1971) 1003; Chem. Abstr., 75 (1971) 118445a

121. Yu. S. Shabasov, L. D. Sychkova, A. N. Kalinichenko And R. Ya. Levina, Zh. Obshch. Khim., 41 (1971) 1599

122. I. D. Rae, Int. J. Sulfur Chem., A, 1 (1971) 59

123. L. I. Khmel'nitskii, T. I. Godovikova, A. V. Igritskaya and S. S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim. (1970) 2108

124. M. L. Poutsma and P. A. Ibarbia, J. Amer. Chem. Soc., 93 (1971) 440

125. R. D. Bach, U. Mazur, R. N. Brummel and L.-H. Lin, J. Amer. Chem. Soc., 93 (1971) 7120

126. R. Vaidyanathaswamy and D. Devaprabhakara, Tetrahedron Lett. (1971) 915

127. F. Toda, N. Ooi and K. Akagi, Bull. Chem. Soc. Japan, 44 (1971) 1050

128. G. Chandra and D. Devaprabhakara, Curr. Sci., 40 (1971) 400; Chem. Abstr., 75 (1971) 98098j

129. H. A. Staab and J. Ipaktschi, Chem. Ber., 104 (1971) 1170

130. D. M. Barlex, R. D. W. Kemmitt and G. W. Littlecott, Chem. Commun. (1971) 199

131. B. L. Dyatkin, L. G. Zhuravkova, B. I. Martynov, E. I. Mysov, S. R. Sterlin and I. L. Knunyants, J. Organometal. Chem., 31 (1971) C15

132. R. D. Bach and D. K. Mitra, Chem. Commun. (1971) 1433

133. D. H. Ballard and A. J. Bloodworth, J. Chem. Soc. C (1971) 945

134. A. J. Bloodworth and R. J. Bunce, J. Chem. Soc. C (1971) 1453

135. P. L. Nayak and M. K. Rout, J. Inst. Chem., Calcutta 43 (Pt. 1) (1971) 32; Chem. Abstr., 75 (1971) 48082d

136. R. D. Bach, R. N. Brummel and R. F. Richter, Tetrahedron Lett. (1971) 2879

137. M. Matsuo and Y. Saito, J. Organometal., 27 (1971) C41

138. G. M. Cree, J. Organometal. Chem., 27 (1971) 1

139. R. Wörle, Erdöl, Kohle, Erdgas, Petrochem. Brennstoff-Chem., 24 (1971) 458

140. M. Takasago, K. Takaoka and M. Seno, Yukagaku, 20 (1971) 415; Chem. Abstr., 75 (1971) 88214e

141. R. Gibbs and W. P. Weber, J. Chem. Educ., 48 (1971) 477

142. H. B. Tinker, J. Organometal. Chem., 32 (1971) C25

143. V. I. Sokolov, V. V. Bashilov and O. A. Reutov, Dokl. Akad. Nauk SSSR, 197 (1971) 101

144. N. V. Stulin and N. I. Putokhin, Khimiya, (1969) 108; Chem. Abstr., 75 (1971) 98652k

145. K. K. Panday and R. Kaushal, Indian J. Appl. Chem., 32 (1969) 94; Chem. Abstr., 75 (1971) 36279k

146. M. Lacova, F. Volna, E. Greiplova and P. Hrnciar, Chem. Zvesti, 24 (1970) 309; Chem. Abstr., 74 (1971) 100188p

147. M. W. Buxton, R. H. Mobbs, and D. E. M. Wotton, J. Fluorine Chem., 1 (1971) 179

148. R. D. Chambers and D. J. Spring, J. Organometal. Chem., 31 (1971) C13

149. A. J. Canty and G. B. Deacon, Austral. J. Chem., 24 (1971) 489

150. S. F. Campbell, J. M. Leach, R. Stephens and J. C. Tatlow, J. Fluorine Chem., 1 (1971) 85

151. G. Wulfsberg and R. West, J. Amer. Chem. Soc., 93 (1971) 4085

152. V. R. Polishchuk, L. S. German and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., (1971) 795

153. V. R. Polishchuk, L. S. German and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 2024

154. V. R. Polishchuk, L. S. German and I. L. Knunyants, Zh. Vses. Khim. Obshchest., 16 (1971) 109; Chem. Abstr., 75 (1971) 36276g

155. V. R. Polishchuk, L. S. German and I. L. Knunyants, Zh. Vses. Khim. Obshchest., 16 (1971) 114; Chem. Abstr., 75 (1971) 20552h

156. L. I. Zakharkin, V. N. Kalinin, I. R. Gol'ding, A. M.

Sladkov and A. V. Grebennikov, Zh. Obshch. Khim., 41 (1971) 823

157. L. I. Zakharkin and N. A. Ogorodnikova, Zh. Obshch. Khim., 41 (1971) 573

158. D. Seyferth, R. S. Marmor and P. Hilbert, J. Org. Chem., 36 (1971) 1379

159. M. Regitz, A. Liedenheger, U. Eckstein, M. Martin and W. Anschütz, Justus Liebigs Ann. Chem., 748 (1971) 207

160. J. Lorberth, J. Organometal. Chem., 27 (1971) 303

161. W. Beck, K. Burger and W. P. Fehlhammer, Chem. Ber., 104 (1971) 1816

162. C. J. Cooksey, D. Dodd and M. D. Johnson, J. Chem. Soc. B (1971) 1380

163. N. A. Nesmeyanov, A. V. Kalinin and O. A. Reutov, Dokl. Akad. Nauk SSSR, 195 (1970) 98

164. G. A. Gray, W. R. Jackson and V. M. A. Chambers, J. Chem. Soc. C (1971) 200

165. V. M. A. Chambers, W. R. Jackson and G. W. Young, J. Chem. Soc. C (1971) 2075

166. T. C. Morrill and F. L. Vandemark, Tetrahedron Lett. (1971) 1811

167. S. F. Zhil'tsov, L. I. Kachaeva and G. G. Petukhov, Zh. Obshch. Khim., 40 (1970) 2042

168. G.G. Petukhov and L. I. Kachaeva, Uch. Zap. Gor'k. Gos. Pedagog. Inst. (1970), No. 123, 270; Chem. Abstr., 76 (1972) 14672b

169. V. R. Polishchuk, L. S. German and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 798

170. J.-J. Perie and A. Lattes, Bull. Chem. Soc. France (1971) 1378

171. M. Lalithambika, S. S. Katiyar and D. Devaprabhakara, J. Electroanal. Chem. Interfacial Electrochem., 31 (1971) 219

172. A. B. Ershler, A. N. Kashin, K. P. Butin and I. P. Beletskaya, Elektrokhim., 7 (1971) 953; Chem. Abstr., 75 (1971) 97990g

173. C. C. Lee and J. Law, Can. J. Chem., 49 (1971) 2746

174. V. Ts. Kampel, K. A. Bilevich and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 197 (1971) 95

175. M. Fleischmann, D. Pletcher and G. Sundholm, J. Electroanal. Chem. Interfacial. Electrochem., 31 (1971) 51

176. B. L. Dyatkin, S. R. Sterlin, B. I. Martynov and I. L. Knunyants, Tetrahedron Lett. (1971) 345

177. J. M. Jerkunica and T. G. Traylor, J. Amer. Chem. Soc., 93 (1971) 6278

178. O. A. Reutov, E. V. Uglova, V. D. Makhaev and V. S. Petrosyan, Zh. Org. Khim., 6 (1970) 2153

179. I. P. Beletskaya, V. B. Vol'eva and O. A. Reutov, Dokl. Akad. Nauk SSSR, 195 (1970) 360

180. I. P. Beletskaya, V. B. Vol'eva, S. V. Rykov, A. L. Buchachenko and A. V. Kessenikh, Izv. Akad. Nauk. SSSR, Ser. Khim. (1971) 454

181. I. P. Beletskaya, L. V. Savinykh and O. A. Reutov, Dokl. Akad. Nauk SSSR, 197 (1971) 1325

182. L. L. Schaleger and Z. Garcia, Chem. Commun. (1971) 373

183. L. V. Pepekina, L. G. Yudin, A. I. Pavlyuchenko, M. I. Vinnik and A. N. Kost, Zh. Org. Khim., 7 (1971) 839

184. M. I. Vinnik, L. V. Pepekina, L. G. Yudin, A. I. Pavlyuchenko and A. N. Kost, Zh. Org. Khim., 7 (1971) 2332

185. I. P. Beletskaya, L. V. Savinykh and O. A. Reutov, J. Organometal. Chem., 26 (1971) 13

186. I. P. Beletskaya, L. V. Savinykh and O. A. Reutov, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 1585

187. I. P. Beletskaya, L. V. Savinykh, V. N. Gulyachkina and O. A. Reutov, J. Organometal. Chem., 26 (1971) 23

188. V. I. Stanko, O. Yu. Okhlobystin, G. A. Anorova and I. P. Beletskaya, Zh. Obshch. Khim., 40 (1970) 2767

189. A. N. Nesmeyanov, E. G. Perevalova, D. A. Lemenovskii, V. P. Alekseev and K. I. Grandberg, Dokl. Akad. Nauk. SSSR, 198 (1971) 1099

190. S. F. Zhil'tsov, L. F. Kudryavtsev, O. N. Druzhkov and G. G. Petukhov, Zh. Obshch. Khim., 40 (1970) 1533

191. G. A. Artamkina, I. P. Beletskaya and O. A. Reutov, Zh. Org. Khim., 7 (1971) 2014

192. T. Sakakibara and Y. Odaira, J. Org. Chem., 36 (1971) 3644

193. V. I. Pakhomov, A. V. Medvedev, V. I. Bregadze and O. Yu. Okhlobystin, J. Organometal. Chem., 29 (1971) 15

194. R. G. Mikaelyan, A. P. Baranov, A. K. Mal'tsev and O. M. Nefedov, Zh. Obshch. Khim., 41 (1971) 1881

195. P. V. Roling, S. B. Roling and M. D. Rausch, Synth. Inorg. Metalorg. Chem., 1 (1971) 97

196. V. Ts. Kampel', K. A. Bilevich and O. Yu. Okhlobystin, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 2103

197. A. N. Nesmeyanov, N. S. Kochetkova, L. A. Fedorov and R. B. Materikova, Dokl. Akad. Nauk SSSR, 199 (1971) 361

198. F. G. Thorpe, T. N. Huckerby, P. H. Lindsay and S. W. Breuer, Tetrahedron Lett. (1971) 2821

199. I. P. Beletskaya, I. I. Zakharycheva and O. A. Reutov, Dokl. Akad. Nauk SSSR, 195 (1970) 837

200. M. D. Johnson, M. H. Abraham, D. Dodd, E. S. Lewis and R. A. More O'Ferrall, J. Chem. Soc. B (1971) 762

201. D. Breitinger, A. Zober and M. Neubauer, J. Organometal. Chem., 30 (1971) C49

202. G. Plazzogna, P. Zanella and L. Doretti, J. Organometal. Chem., 29 (1971) 169

203. H. Leimeister and K. Dehnicke, J. Organometal. Chem., 31 (1971) C3

204. A. F. Shihada and K. Dehnicke, J. Organometal. Chem., 26 (1971) 157

205. W. Thiel, F. Weller, J. Lorberth and K. Dehnicke, Z. anorg. allg. Chem., 381 (1971) 57

206. V. I. Buzulukov and V. P. Maslennikov, Zh. Obshch. Khim., 41 (1971) 1881

207. J. L. Wardell, R. D. Taylor and T. J. Lillie, J. Organometal. Chem., 33 (1971) 25

208. A. I. Busev, L. I. Teternikov, Y. A. Mittsel and V. K. Akimov, Zh. Obshch. Khim., 41 (1971) 1730

209. N. K. Bliznyuk, L. D. Protasova and Z. N. Kvasha, USSR patent 282,315 (1970); Chem. Abstr., 75 (1971) 6084a

210. I. A. Vostokov and V. T. Bychkov, Zh. Obshch. Khim., 41 (1971) 838

211. A. G. Davies and P. G. Harrison, J. Chem. Soc. C (1971) 1769

212. J. Lorberth and F. Weller, J. Organometal. Chem., 32 (1971) 145

213. K. Seppelt and W. Sundermeyer, Chem. Ber., 103 (1971) 3939

214. S. F. Zhil'tsov and V. M. Kashin, Zh. Obshch. Khim., 41 (1971) 2103

215. R. J. Kline, L. F. Sytsma and D. R. Shackle, Inorg. Nucl. Chem. Lett., 7 (1971) 311

216. D. Horton and C. G. Tindall, Jr., Carbohyd. Res., 17 (1971) 240

217. D. N. Kravtsov, L. A. Fedorov, A. S. Peregudov and A. N. Nesmeyanov, Dokl. Akad. Nauk SSSR, 196 (1971) 110

218. W. K. Glass and J. O. McBreen, Inorg. Nucl. Chem. Lett., 7 (1971) 733

219. W. Sundermeyer, A. Roland and K. Seppelt, Angew. Chem., 83 (1971) 443

220. P. G. Cookson and G. B. Deacon, Austral. J. Chem., 24 (1971) 935

221. S. Suzuki and K. Sugita, Bull. Chem. Soc. Japan, 44 (1971) 641

222. A. M. Kiwan and H. M. N. H. Irving, Anal. Chem. Acta, 54 (1971) 351

223. T. Nowicka-Jankowska and H. M. N. H. Irving, Anal. Chim. Acta, 54 (1971) 489

224. G. S. Kalinina, O. A. Kruglaya, B. I. Petrov and N. S. Vyazankin, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 2101

225. T. F. Schaaf and J. P. Oliver, J. Organometal. Chem., 32 (1971) 307

226. T. F. Schaaf and J. P. Oliver, Inorg. Chem., 10 (1971) 1521

227. N. S. Vyazankin, O. A. Kruglaya, B. I. Petrov, A. N. Egorochkin and Ya. S. Khorshev, Zk. Obshch. Khim., 40 (1970) 1279

228. O. A. Kriuglaya, Yu. I. Baukov, B. I. Petrov and N. S. Vyazankin, Zh. Obshch. Khim., 41 (1971) 1408

229. Yu. A. Aleksandrov, G. A. Razuvaev, V. N. Glushkova and V. Ya. Savukova, J. Organometal. Chem., 27 (1971) 201

230. V. N. Glushkova and Yu. A. Aleksandrov, Zh. Obshch. Khim. 41 (1971) 1751

231. V. T. Bychkov, G. A. Abakumov, N. S. Vyazankin and G. A. Razuvaev, Izv. Akad. Nauk SSSR, Ser. Khim. (1971) 892

232. V. T. Bychkov, N. S. Vyazankin and G. A. Razuvaev, Zh. Obshch. Khim., 41 (1971) 716

233. S. W. Bennett, C. Eaborn, R. A. Jackson and R. W. Walsingham, J. Organometal. Chem., 27 (1971) 195

234. R. Fields, R. N. Haszeldine and P. J. Palmer, Tetrahedron Lett. (1971) 1879

235. R. Fields, R. N. Haszeldine and A. F. Hubbard, J. Chem. Soc. C (1971) 3838

236. S. W. Bennett, C. Eaborn, R. A. Jackson and R. Pearce, J. Organometal. Chem., 28 (1971) 59

237. E. N. Gladyshev, N. S. Vyazankin, V. S. Andreevichev, A. A. Klimov and G. A. Razuvaev, J. Organometal. Chem., 28 (1971) C42

238. M. N. Bochkarev, L. P. Maiorova, A. I. Charov and N. S. Vyazankin, Zh. Obshch. Khim., 41 (1971) 1408

239. E. N. Gladyshev, N. S. Vyazankin, Yu. A. Sorokin, V.I. Ermolaev, G. N. Bortnikov and G. A. Razuvaev, Dokl. Akad. Nauk SSSR, 194 (1970) 1083

240. A. F. Clemmit and F. Glockling, J. Chem. Soc. A (1971) 1164

241. K. A. Hooton, J. Chem. Soc. A (1971) 1251

242. V. I. Ermolaev, Yu. A. Sorokin, E. N. Gladyshev, N. S. Vyazankin and G. A. Razuvaev, Zh. Obshch. Khim., 41 (1971) 1878

243. D. Breitinger, K. Geske and W. Beitelschmidt, Angew. Chem., 83 (1971) 577

244. N. N. Greenwood and N. F. Travers, J. Chem. Soc. A (1971) 3257

245. N. N. Greenwood, J. A. McGinnety and J. D. Owen, J. Chem. Soc. A (1971) 809

246. A. J. Canty and B. M. Gatehouse, Chem. Commun. (1971) 443

247. J. L. Bribes and R. Gaufrès, Spectrochim. Acta, 27A (1971) 2133

248. J. Mink and Yu. A. Pentin, Acta Chim. Acad. Sci. Hung., 67 (1971) 435

249. J. Mink and Yu. A. Pentin, Acta Chim. Acad. Sci. Hung., 66 (1970) 277

250. E. Samuel and M. Bigorgne, J. Organometal. Chem., 30 (1971) 235

251. Z. Meić and M. Randić, J. Mol. Spectroscopy, 39 (1971) 39

252. N. A. Dao and D. Breitinger, Spectrochim. Acta, 27A (1971) 905

253. J. Mink and L. Nemes, J. Organometal. Chem., 28 (1971) C39

254. J. L. Bribes and R. Gaufrès, J. Mol. Struct., 9 (1971) 423

255. P. J. Banney and P. R. Wells, Austral. J. Chem., 24 (1971) 317

256. L. A. Fedorov, V. N. Kalinin, K. G. Gasanov and L. I. Zakharkin, Zh. Org. Khim., 7 (1971) 432

257. R. B. Johannesen and R. W. Duerst, J. Magn. Resonance, 5 (1971) 355

258. A. P. Ebdon, T. N. Huckerby and F. G. Thorpe, Tetrahedron Lett. (1971) 2921

259. C. H. Campbell and M. L. H. Green, J. Chem. Soc. A (1971) 3282

260. W. McFarlane, Chem. Commun. (1971) 609

261. S. W. Breuer, T. E. Fear, P. H. Lindsay and F. G. Thorpe, J. Chem. Soc. C (1971) 3519

262. S. C. Cohen, J. Chem. Soc. A (1971) 1571

263. S. C. Cohen, J. Chem. Soc. A (1971) 632

264. D. J. Harvey, M. G. Horning and P. Vouros, Org. Mass Spec., 5 (1971) 599

265. A. C. LaLonde and S. J. W. Price, Can. J. Chem., 49 (1971) 3367

266. E. Vander Donckt and C. Vogels, Spectrochim. Acta, 27A (1971) 2157

267. A. I. Busev and L. I. Teternikov, Anal. Lett. (1971) 53

268. D. Monnier and A. Gorgia, Anal. Chim. Acta 54 (1971) 497

269. D. Monnier and A. Gorgia, Anal. Chim. Acta 54 (1971) 505

270. A. Gorgia and D. Monnier, Anal. Chim. Acta 55 (1971) 247

271. W. Haerdi, E. Gorgia and N. Lakhoua, Helv. Chim. Acta, 54 (1971) 1497

272. S. L. Law, Science, 174 (1971) 285

273. R. Klein and S. Herman, Science, 172 (1971) 872

274. G. F. Wright, Science, 174 (1971) 771

275. L. Landner, Nature, 230 (1971) 453

276. A. L. Hammond, Science, 171 (1971) 788