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ORGANOMERCURIALS IN ORGANIC SYNTHESIS

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Organomercurials are among the oldest organometallics known, having first been reported in 1852 by Frankland.[1] In the next sixty years new routes to organomercurials were discovered and many applications in synthesis were reported, particularly in the preparation of other organometallics. However, with the discovery of the versatile Grignard reagent, interest in organomercurials waned. Only in recent years have these unique organometallics received renewed attention, due in large part to their ability to accommodate essentially all important organic functional groups and the ease with which they undergo transmetallation to form transition metal organometallics useful in organic synthesis.

This report considers the many applications of organomercurials in organic synthesis, first briefly recounting the wide variety of methods available for the preparation of organomercurials. This will be done in the following section, but the reader is encouraged to consult the two major books in this area for details.[2,3] Subsequent sections will cover the many reactions of organomercurials which should be of interest to the synthetic organic chemist. However, two areas of major importance have been purposely omitted. The use of organomercurials as divalent carbon transfer reagents will not be discussed here, since several earlier reviews are available.[4-6] Unfortunately, the highly valuable solvomercuration–demercuration reaction has not similarly been reviewed in recent years, but its scope cannot be accommodated by the present review and it is thus omitted. An all-encompassing review of the above topics is forthcoming in a book entitled *Organomercury Compounds in Organic Synthesis* soon to be published by the present author.

1. PREPARATION OF ORGANOMERCURIALS

Numerous methods are available for the preparation of organomercurials. One of the more obvious approaches, the direct reaction of organic halides and metallic mercury (eqn 1), is only of limited utility,

$$\text{R–X} + \text{Hg} \longrightarrow \text{RHgX} \tag{1}$$

since it only works well for methyl iodide,[7] methylene iodide[8-10] and other polyhalomethanes[11] and perfluoroalkyl halides,[12-14] allylic halides,[15,16] propargyl iodide,[17] benzylic halides[18,19] and perfluoroaryl iodides.[20,21] However, the use of mercury-sodium amalgams generally gives good yields of diorganomercurials from a wide variety of alkyl[22,23] and aryl[24,25] halides (eqn 2). Electrochemical reduction of organic halides at a mercury cathode also provides diorganomercurials often in excellent yield (eqn 3).[26-29]

$$\text{R–X} + \text{Hg(Na)} \longrightarrow \text{HgR}_2 \tag{2}$$

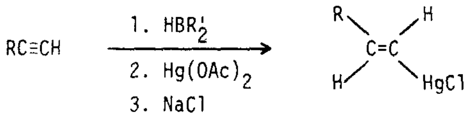
$$\mathrm{R\text{-}X} \xrightarrow{\text{Hg cathode}} \mathrm{HgR_2} \qquad (3)$$

Organomercurials are also readily prepared from a variety of other organometallic reagents. Organomagnesium and -lithium compounds have frequently been employed for this purpose, but this approach is of little interest with regards to this review since these organometallics accommodate little functionality and themselves undergo a number of useful synthetic transformations which necessarily limit the synthetic utility of the resulting organomercurials.

Organoboranes are more useful for the preparation of organomercurials from an organic synthesis viewpoint.[30] Alkyl, benzylic, vinyl and aryl groups are readily transferred from boron to mercury upon treating organoboranes with a wide variety of mercury salts (eqn 4). Boronic and borinic acids and esters, triorganoboranes and tetraorganoborate salts all undergo this reaction. Since organoboranes are directly available via hydroboration of alkenes and alkynes, this approach takes on added significance (eqns 5–7).

$$\mathrm{R\text{-}B}\langle + \mathrm{HgX_2} \longrightarrow \mathrm{RHgX} \qquad (4)$$

$$\mathrm{RCH{=}CH_2} \xrightarrow[\substack{2.\ \mathrm{Hg(OAc)_2} \\ 3.\ \mathrm{NaCl}}]{1.\ \mathrm{HBR'_2}} \mathrm{RCH_2CH_2HgCl} \qquad (5)^{31}$$



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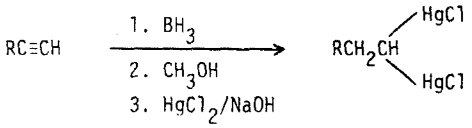


$$\mathrm{RC{\equiv}CH} \xrightarrow[\substack{2.\ \mathrm{CH_3OH} \\ 3.\ \mathrm{HgCl_2/NaOH}}]{1.\ \mathrm{BH_3}} \mathrm{RCH_2CH(HgCl)_2}$$

(7)[34]

Few other organometallic reagents have proven as useful as those of magnesium, lithium or boron for the preparation of organomercurials. While, transmetallation reactions involving organoaluminum, -silicon, -tin, -lead, -zinc, and -palladium appear to possess synthetic utility, few of these organometallics are readily available via procedures which are sufficiently unique that their subsequent conversion to organomercurials would have a synthetic advantage over the other methods outlined in this section.

The ease with which many organic substrates can be directly mercurated provides the real impetus for using organomercurials in organic synthesis. For example, mercury salts react directly with carbon monoxide and alcohols or amines to provide carboalkoxy[35,36] or carboxamido[37,38] mercurials (eqns 8, 9).

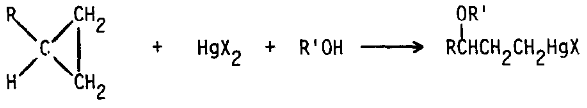
$$\mathrm{Hg(OAc)_2 + ROH + CO \longrightarrow AcOHg\overset{\displaystyle O}{\overset{\|}{C}}OR} \qquad (8)$$

$$\mathrm{Hg(OAc)_2 + 2R_2NH + CO \longrightarrow Hg(\overset{\displaystyle O}{\overset{\|}{C}}NR_2)_2} \qquad (9)$$

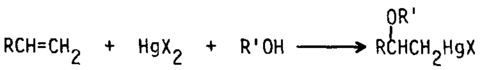
Many organic substrates bearing relatively acidic carbon-hydrogen bonds can also undergo direct mercuration (eqn 10). Organic compounds which have been mercurated in this fashion include cyclopentadiene[39–41] and a variety of ketones,[42–46] nitriles,[46–48] nitro[49,50] and diazo[51,52] compounds. A number of organomercurials have also been prepared by mercuration of C–H containing compounds activated by two or more ketone, acid, ester, amide, nitro, sulfone, phosphonate or cyano groups.

$$R\text{-}H + HgX_2 \longrightarrow RHgX \qquad (10)$$

Gamma substituted alkylmercuric salts are readily available from the reaction of mercury(II) salts, nucleophilic solvents and cyclopropanes (eqn 11).[53] Numerous alkylmercurials have been prepared in this manner and the mechanism of this reaction has been extensively studied.


(11)

The mercuration of alkenes forms the basis of the well-known solvomercuration reaction (eqn 12).

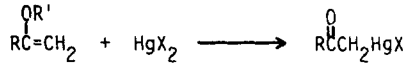


$$RCH{=}CH_2 + HgX_2 + R'OH \longrightarrow RCH(OR')CH_2HgX \qquad (12)$$

However, under certain conditions vinylmercurials can be isolated directly from this type of reaction (eqn 13).[54–58] Under basic conditions di-[59] and trichloroethylenes[60,61] can be mercurated in similar fashion (eqn 14). On the other hand, the mercuration of enol silanes,[62] phosphates,[63] acetates[64,65] or ethers[66,67] provides an invaluable approach to mercurated carbonyl compounds (eqn 15).

$$Ar_2C{=}CH_2 + HgX_2 \longrightarrow Ar_2C{=}CHHgX \qquad (13)$$

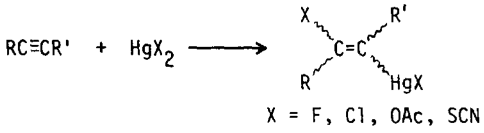
$$Cl_2C{=}CHCl + Hg(CN)_2 + KOH \longrightarrow (Cl_2C{=}CCl)_2Hg \qquad (14)$$



$$RC(OR'){=}CH_2 + HgX_2 \longrightarrow RC(O)CH_2HgX \qquad (15)$$

The mercuration of alkynes proceeds via two entirely different pathways depending on the alkyne and the reaction conditions employed. Under basic conditions terminal alkynes give excellent yields of dialkynylmercurials (eqn 16).[68] In neutral or acidic media, terminal and internal alkynes often add mercury salts to afford vinylmercurials (eqn 17). Alkynes reported to add mercuric halides include acetylene;[69] propyne;[70] cyclooctyne;[71] vinylacetylene;[70,72] alkynyl ethers;[73] propargylic alcohols[74,75] and halides;[74,76] and α,β-unsaturated ketones,[77] acids[78,79] and esters.[78,80,81] Mercuric acetate[82,83] and thiocyanide[84] also add to a variety of internal alkyl or aryl acetylenes to generate vinylmercurials.

$$2\ RC{\equiv}CH \longrightarrow (RC{\equiv}C)_2Hg \qquad (16)$$


(17)

Certainly one of the most important routes to organomercurials is the direct electrophilic aromatic mercuration of arenes (eqn 18). This approach requires only simple electrophilic mercury salts and the corresponding arene. Yields are usually high and substantial functionality is accommodated. Although isomeric mixtures can result, pure isomers are often available via simple recrystallization. Many hundreds of arylmercurials have been prepared by this approach including numerous mercurated alkylbenzenes, haloarenes, phenols, anilines, aryl ethers, nitroarenes and other mono- and polysubstituted arenes. With highly reactive arenes or under forcing reaction conditions, polymercurated products can often be obtained. A large number of polynuclear aromatic mercurials are also available via

$$ArH + HgX_2 \longrightarrow ArHgX \qquad (18)$$

electrophilic mercuration. Mercurated aromatic heterocycles have been obtained from furans, thiophenes, oxazoles, thiazoles, pyridines, quinolines and a variety of other oxygen, nitrogen, sulfur and selenium containing heterocycles. A number of aromatic organometallics, particularly ferrocenes, readily yield organomercurials via direct mercuration.

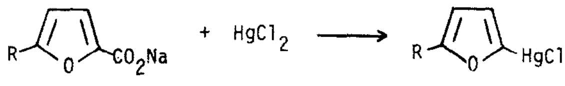
Arylmercurials are also easily prepared from the corresponding aryldiazonium salts by treatment with mercuric chloride and a reducing agent (eqn 19). Copper powder has commonly been employed,[85]

$$ArN_2X + HgX_2 \longrightarrow [ArN_2][HgX_3] \longrightarrow ArHgX \qquad (19)$$

although tin(II) chloride,[86] cupric chloride plus diethyl phosphite,[87] or even metallic mercury[88] work well. When these reactions are run in ammonia, symmetrization occurs and diarylmercurials are isolated.[89] This approach to arylmercurials has the advantage that it results in functionally substituted arylmercurials free of isomers common in many direct electrophilic mercuration reactions.

The decarboxylation of mercury carboxylates provides yet another useful approach to a wide variety of organomercurials (eqn 20). Decarboxylation can be effected either thermally, electrolytically, photochemically or through free radical processes. For example, the attempted mercuration of certain furan or thiophene carboxylic acids affords the corresponding mercurated heterocycle directly (eqn 21). Decarboxylation of substituted benzoic acids usually requires elevated temperatures and affords diarylmercurials.[91,92] Electron withdrawing substituents facillitate decarboxylation. Phthalic and higher polynuclear aromatic dicarboxylic acids behave similarly.[93,94] This approach only proves useful for the synthesis of alkylmercurials when strong electron withdrawing groups are present in the carboxylic acid moiety. Polyhalomethylmercurials, useful as divalent carbon transfer reagents have been prepared in this manner, as have α-mercurated ketones (eqn 22).[95] Alkylmercury carboxylates can also be obtained by photochemical means (eqn 23).[96,97] A free radical chain mechanism has been proposed.[98] Consistent with this is the fact that a variety of peroxides can also be used to initiate these reactions. Yields of organomercurials are generally significantly higher using this approach.

$$(RCO_2)_2Hg \longrightarrow RHgO_2CR \qquad (20)$$



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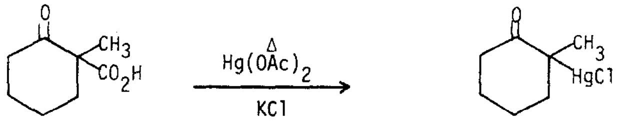


(22)

$$(RCO_2)_2Hg \xrightarrow{h\nu} RHgO_2CR \qquad (23)$$

Sulfinic and sulfonic acids or the corresponding alkali metal salts react with a variety of mercury(II) salts with elimination of SO_2 or SO_3 to form organomercurials. The sulfinic acid reaction, first reported by Peters in 1905,[99] affords high yields of arylmercuric salts or diarylmercurials depending on the stoichiometry (eqn 24).[100–102] Alkylsulfinic acids also react, but the yields of alkylmercurials are lower.

$$RSO_2H(Na) + HgX_2 \longrightarrow RHgX \qquad (24)$$

This approach suffers the disadvantage of requiring starting materials that are not readily available nor easily prepared. Analogous sulfur trioxide elimination from mercury sulfonates is much more limited, since only fully halogenated aryl sulfonic acids give good yields of the corresponding diarylmercurials.[103–105]

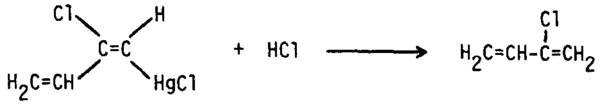
This necessarily brief discussion of the more important methods of preparing organomercurials indicates the diversity of organomercurials available and the wide variety of preparative procedures which can be employed for their synthesis. In the following sections, the major reactions of synthetic interest which these compounds undergo will be surveyed.

2. HYDROGEN AND HALOGEN SUBSTITUTION

Substitution of mercury in organomercurials by hydrogen and halogen has been extensively studied and a number of reviews[106–109] and one book[110] have appeared on the subject. The primary emphasis of most of this work has been on studying the mechanism of electrophilic aliphatic substitution. Our concern here will be on possible synthetic applications of these reactions.

The protonolysis of organomercury compounds, although extensively studied from a mechanistic standpoint, has found relatively little synthetic utility. The most important application of this reaction would appear to be the isotopic labelling of organic substrates. Unfortunately, deuterolysis of dialkylmercurials proceeds with significant racemization. However, the protonolysis or deuterolysis of alkenylmercurials derived from mercury salt additions to alkynes provides a valuable method of preparing stereoisomerically pure alkenes (eqns 25–28). Similarly, sodium borohydride reduction of β-acetoxymercurials derived from alkyne additions can be non-stereospecifically reduced to the corresponding enol acetates (eqn 29).[112]

$$\underset{\text{cis or trans}}{\mathrm{ClCH{=}CHHgCl}} + \mathrm{DCl} \longrightarrow \underset{\text{retention}}{\mathrm{ClCH{=}CHD}} \qquad (25)^{111}$$



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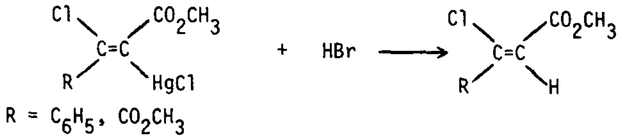
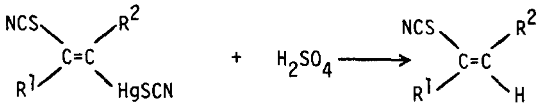
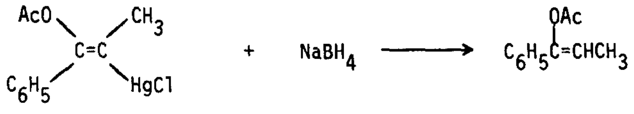


(27)[78]



(28)[84]

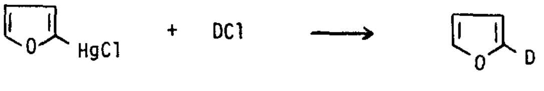


(29)

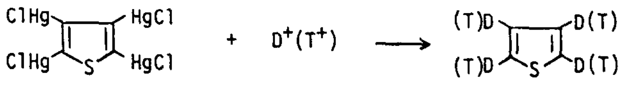
Deuterolysis of readily available dialkynylmercury compounds provides a convenient route to labelled acetylenes (eqn 30).[113]

$$(\mathrm{CH_3C{\equiv}C})_2\mathrm{Hg} + 2\ \mathrm{DCl} \longrightarrow 2\ \mathrm{CH_3C{\equiv}CD} \qquad (30)$$

Heterocycles, organometallics and even mono- and polynucleotides have also been isotopically labelled via substitution of the corresponding organomercurials (eqns 31–34).



(31)[114]



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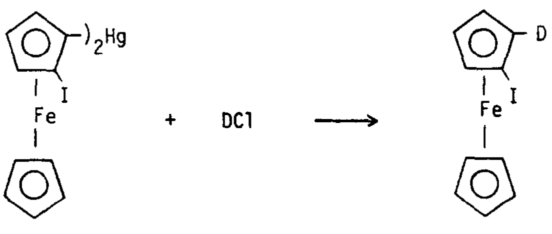

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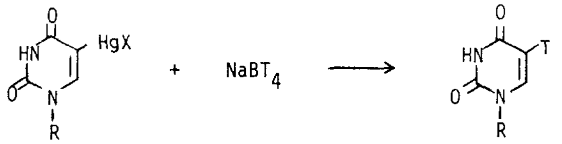
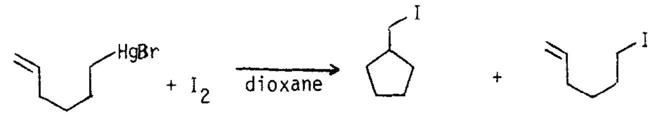

(34)[118]

The halogenation of organomercurials provides a useful method for the preparation of a wide variety of organic halides, especially those not easily obtained by direct halogenation. This reaction has also proven invaluable for determining the position of mercury in an organomercurial of unknown structure. It is most commonly effected by employing the halogens themselves (eqns 35, 36), although a number of other reagents to be mentioned later have been employed.

$$R_2Hg + X_2 \longrightarrow RHgX + R\text{-}X \qquad (35)$$

$$RHgX + X_2 \longrightarrow HgX_2 + R\text{-}X \qquad (36)$$

The halogenation of alkylmercurials has been extensively studied,[110] although primarily from a mechanistic standpoint. Depending on the structure of the alkylmercurial, the specific reagent employed, the solvent polarity and the presence or absence of air or light, one can observe either free radical or electrophilic processes. Free radical processes can of course lead to racemized or even rearranged products as evident in the following example (eqn 37).[119] Bromine is less prone than iodine to undergo free radical reactions and at −65° in pyridine it halogenates simple alkylmercuric halides with a high degree of retention.[120] The importance of reaction conditions is evident in the following interesting example (eqn 38).[121] These halogenation reactions can prove very useful when employed in combination with the solvomercuration reaction (eqns 39–41). In certain cases halogenation does not proceed readily and other means must be found to effect reaction. For example, polyfluorinated alkylmercurials require temperatures of 200–300°.[125] Alkylmercurials bearing several gamma nitro groups are also unreactive towards electrophilic halogenation, but can be brominated in high yield using free radical conditions (eqn 42).[126]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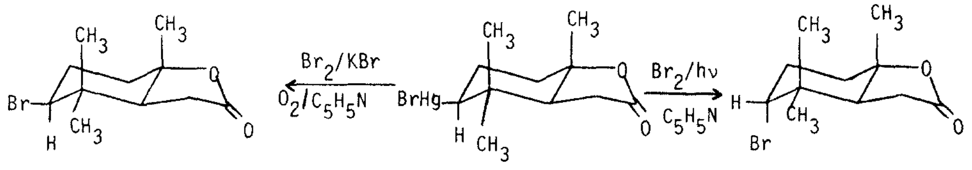
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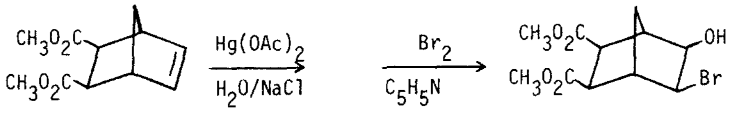
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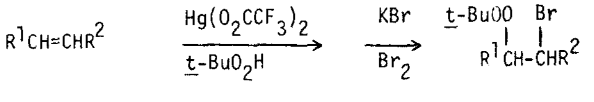
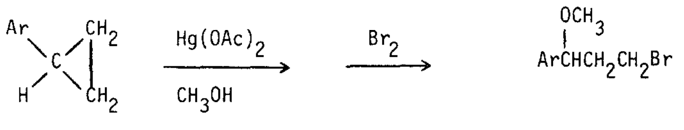
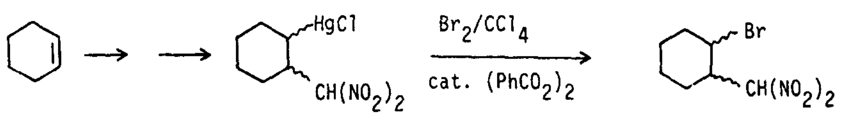

$$R^1CH{=}CHR^2 \xrightarrow[\underline{t}\text{-}BuO_2H]{Hg(O_2CCF_3)_2} \xrightarrow[Br_2]{KBr} \overset{\underline{t}\text{-}BuOO}{R^1CH}\text{-}\overset{Br}{CHR^2} \qquad (40)^{123}$$


(41)[124]



(42)

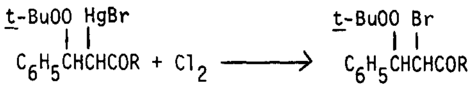
The hydroboration–mercuration of terminal olefins and subsequent *in situ* bromination affords a convenient method for the anti-Markovnikov hydrobromination of olefins (eqn 43).[127] Internal olefins

$$\mathrm{RCH{=}CH_2} \xrightarrow{1/3\ \mathrm{BH_3}} \xrightarrow{\mathrm{Hg(OAc)_2}} \xrightarrow{\mathrm{Br_2}} \underset{71\text{-}86\%}{\mathrm{RCH_2CH_2Br}} \qquad (43)$$

give greatly reduced yields. Although direct iodination produces alkyl acetates (see Section 3), if one adds methanol prior to iodination or uses dicyclohexylborane instead of diborane, one can obtain excellent yields of primary alkyl iodides by this same sequence (eqn 44).[128] However, equally convenient procedures now exist for the direct bromination or iodination of organoboranes.

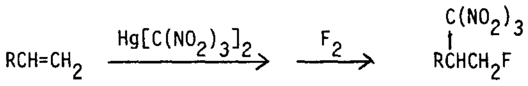
$$\mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{(C_6H_{11})_2BH}} \xrightarrow{\mathrm{Hg(OAc)_2}} \xrightarrow{\mathrm{I_2}} \mathrm{RCH_2CH_2I} \qquad (44)$$

The chlorination and fluorination of alkylmercurials have received only very limited attention. Rearrangements have been observed during chlorination and the chlorination of alkylmercuric bromides has been observed to proceed with halogen exchange (eqn 45).[129] Fluorination studies have been



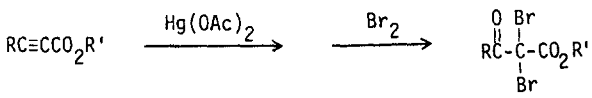
$$\mathrm{C_6H_5\overset{\underline{t}\text{-}BuOO}{\overset{|}{C}}H\overset{HgBr}{\overset{|}{C}}HCOR} + \mathrm{Cl_2} \longrightarrow \mathrm{C_6H_5\overset{\underline{t}\text{-}BuOO}{\overset{|}{C}}H\overset{Br}{\overset{|}{C}}HCOR} \qquad (45)$$

confined to the adducts derived from olefins and *bis*-(trinitromethyl)mercury (eqn 46).[130]

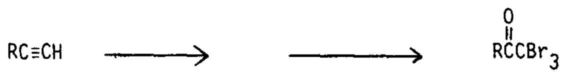


$$\mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{Hg[C(NO_2)_3]_2}} \xrightarrow{\mathrm{F_2}} \mathrm{R\overset{C(NO_2)_3}{\overset{|}{C}}HCH_2F} \qquad (46)$$

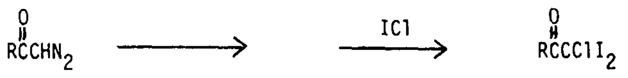
A number of benzylic and functionally substituted organomercurials also undergo facile halogenation. The following examples portend a certain synthetic utility (eqns 47–49).



$$\mathrm{RC{\equiv}CCO_2R'} \xrightarrow{\mathrm{Hg(OAc)_2}} \xrightarrow{\mathrm{Br_2}} \mathrm{R\overset{O}{\overset{\|}{C}}\text{-}\underset{\underset{Br}{|}}{\overset{Br}{\overset{|}{C}}}\text{-}CO_2R'} \qquad (47)^{131}$$



$$\mathrm{RC{\equiv}CH} \longrightarrow \longrightarrow \mathrm{R\overset{O}{\overset{\|}{C}}CBr_3} \qquad (48)^{131}$$

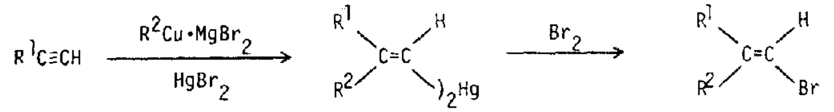


$$\mathrm{R\overset{O}{\overset{\|}{C}}CHN_2} \longrightarrow \xrightarrow{\mathrm{ICl}} \mathrm{R\overset{O}{\overset{\|}{C}}CClI_2} \qquad (49)^{132}$$

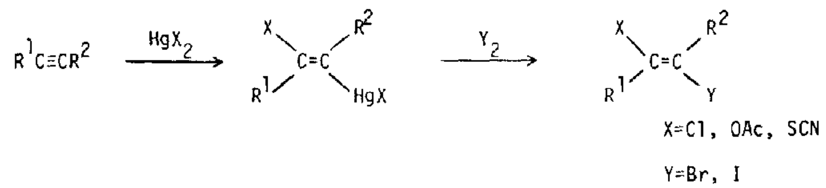
The halogenation of vinylmercurials provides a valuable method for the preparation of vinyl halides as seen by the following examples (eqns 50–54). Note that all these alkenyl halides have been prepared from alkenes or alkynes in only two steps.

$$\mathrm{Cl_2C{=}CHCl} \xrightarrow[\mathrm{NaOH}]{\mathrm{Hg(CN)_2}} \mathrm{(Cl_2C{=}CCl)_2Hg} \xrightarrow{\mathrm{X_2}} \underset{\mathrm{X{=}Cl,\ Br,\ I}}{\mathrm{Cl_2C{=}CClX}} \qquad (50)^{133}$$

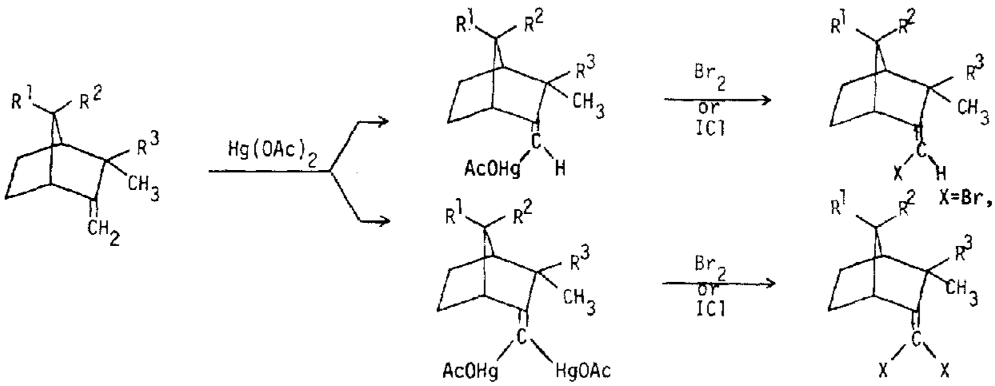
$$\mathrm{HC{\equiv}CH} \xrightarrow[\mathrm{NH_3}]{\mathrm{HgCl_2}} \underset{\text{cis or trans}}{\mathrm{(ClCH{=}CH)_2Hg}} \xrightarrow{\mathrm{Cl_2}} \mathrm{ClCH{=}CHCl} \qquad (51)^{134}$$



(52)[135]

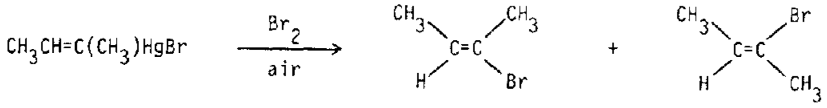


(53)[70,74,84,112,136]



(54)[58]

Only in a few cases has the stereochemistry of the halogenation of vinylmercurials been closely examined. The iodination of *cis*- and *trans*-β-chloro-vinylmercuric chloride, and the bromination of *cis*- and *trans*-styrylmercuric bromide have both been observed to proceed with complete retention in polar solvents, but to give mixtures of stereoisomers in non-polar solvents or under photochemical stimulation.[136–139] At the time, free radicals were assumed responsible for isomerization. More recently, however, it has been reported that while alkenylmercuric bromides react with bromine in pyridine in the presence of air with almost complete retention, bromine in carbon disulfide in the presence of air gives predominant inversion (eqn 55).[140] A mechanism involving trans addition of bromine to the carbon–carbon double bond, followed by trans elimination of mercuric bromide was suggested. This ability to control the stereochemistry in the bromination of alkenylmercurials makes this a particularly attractive route to alkenyl bromides, especially in view of the ease with which these organomercurials can now be prepared directly from alkynes via hydroboration-mercuration.



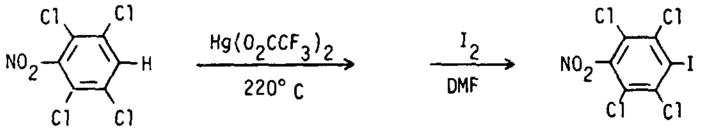
(55)

E/C_5H_5N	99.6	:	0.4
E/CS_2	12	:	88
Z/C_5H_5N	8.1	:	91.9
Z/CS_2	93	:	7

The halogenation of alkynylmercurials provides a very simple route to alkynyl halides (eqn 56).[141–144]

$$RC{\equiv}CH \longrightarrow (RC{\equiv}C)_2Hg \xrightarrow{X_2} RC{\equiv}CX \quad X{=}Cl,\ Br,\ I \qquad (56)$$

The halogenation of aromatic organomercurials has been a widely employed reaction. It has been used as an analytical tool to determine the ratio of arylmercuric iodide and diarylmercurial formed in a reaction, studied mechanistically, employed in the structure determination of many an arylmercurial, and utilized to synthesize a wide variety of aromatic halides. Synthetically, the preparation of aryl halides via halogenation of arylmercurials offers a number of synthetic advantages over other approaches. Where direct halogenation may result in isomeric mixtures, one can frequently isolate directly or by simple recrystallization procedures isomerically pure arylmercurials which can be subsequently halogenated to afford isomerically pure aryl halides. A further advantage is that many arenes undergo mercuration–halogenation, which will not undergo direct halogenation (eqn 57).[145] One can also take advantage of the wide variety of methods available for the synthesis of arylmercurials (eqns 58–60). Note in this last example that it is not necessary to isolate the arylmercurial. In fact, thermolysis of mercury aryldiazonium salts in the presence of excess alkali metal halide affords good yields of the aryl halide directly. This approach has proven useful in those cases where the Sandmeyer approach fails.



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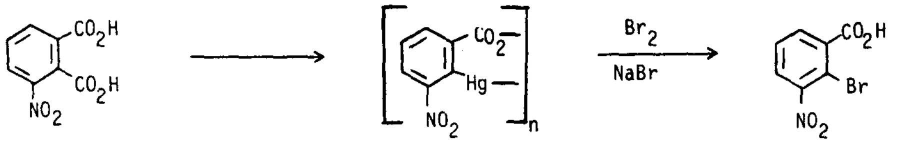

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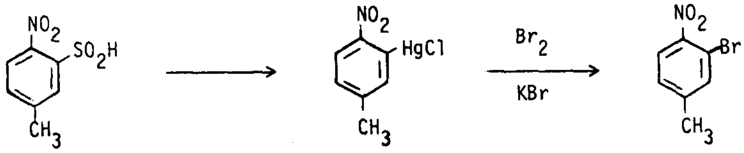
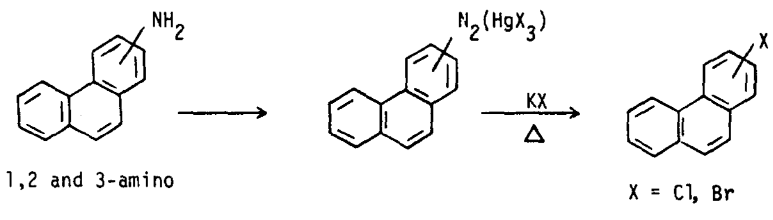
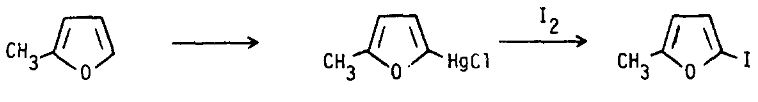


(59)[147]

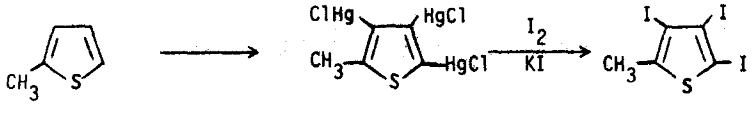


(60)[148]

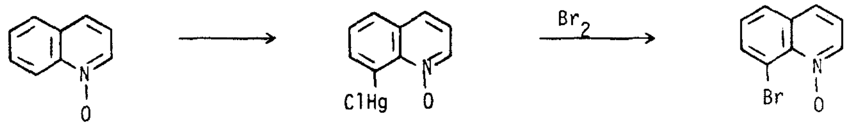
The mercuration–halogenation of heterocycles and organometallics has also proven quite useful (eqns 61–66).



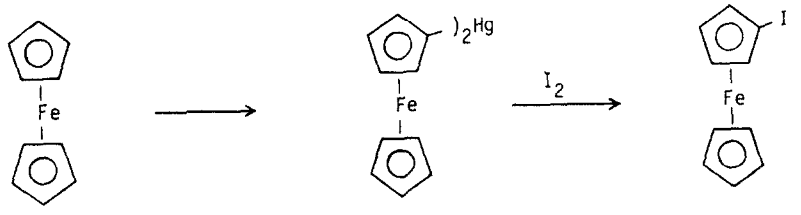
(61)[90]



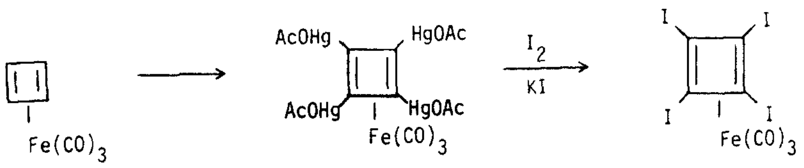
(62)[149]



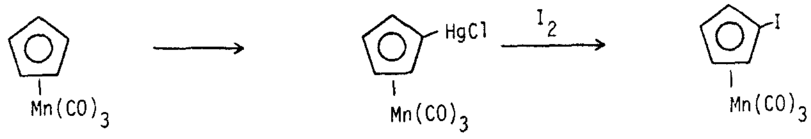
(63)[150]



(64)[151]

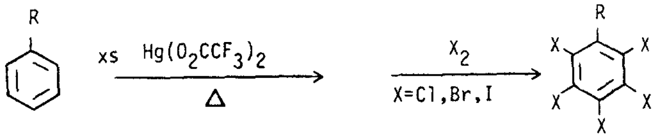


(65)[152]



(66)[153]

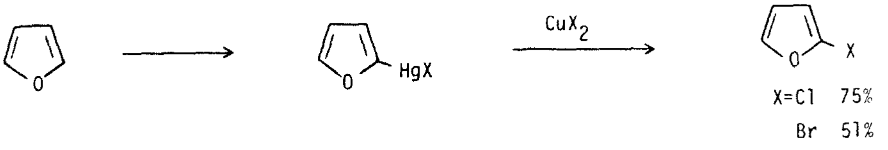
The polyhalogenation of aromatic compounds can also be conveniently effected by using highly electrophilic mercury salts in excess, followed by halogenation (eqn 67).[154–158] This is one of the simplest approaches to polyhaloaromatics.



(67)

R=H, NH_2, NHAc, CH_3O, CH_3, CF_3, F, Cl, Br, NO_2, CO_2H, CO_2Na, $CONH_2$

Several halogen-containing reagents, other than the elements themselves, have also found use in the halogenation of organomercurials. The mixed halogens ICl and IBr are useful iodinating agents. Haloimides, particularly *N*-bromosuccinimide, have occasionally been employed. Cupric(II) chloride and bromide in a polar solvent will halogenate a wide variety of organomercurials. This approach provides an important route to bromofurans since neither furans nor mercurated furans can be brominated directly with bromine (eqn 68).[159] No other halogenating agents have found as widespread utility as those mentioned above.



(68)

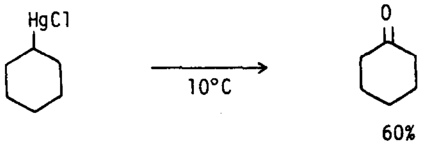
In conclusion, virtually every type of alkyl-, alkenyl-, alkynyl-, aryl-, heterocyclic or organometallic halide can be obtained from the corresponding organomercurial using direct halogenation with chlorine, bromine or iodine. Where these reagents fail, *N*-bromosuccinimide or cupric halides often work. With the many unique methods now available for the preparation of organomercurials, one can expect to see increasing application of this approach to the synthesis of organic halides.

3. SYNTHESIS OF HETEROATOM-CONTAINING COMPOUNDS

A wide variety of heteroatom-containing compounds can be conveniently prepared via organomercury intermediates. Some of the more interesting and useful approaches to the synthesis of oxygen-, sulfur-, nitrogen-, and phosphorus-containing compounds will be discussed in this section in the order indicated.

While most organomercurials are quite stable to oxygen, ozone reacts rapidly with alkylmercurials even at low temperatures (eqns 69–71).[160] The oxidation of secondary alkylmercurials appears quite

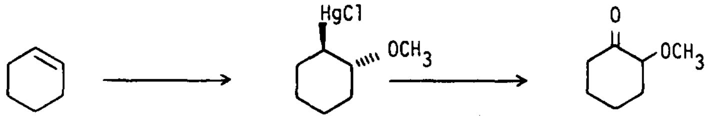
$$(\underline{n}\text{-}C_6H_{13})_2Hg \xrightarrow[-76°C]{O_3} \underset{80\%}{2\ \underline{n}\text{-}C_5H_{11}CO_2H} \tag{69}$$



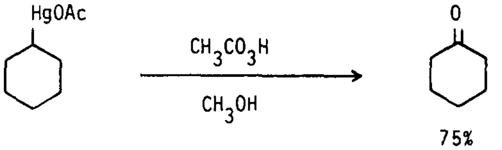
(70)

$$(CH_3)_3CHgCl \xrightarrow[10°C]{} \underset{50\%}{(CH_3)_3COH} \tag{71}$$

useful for the synthesis of α-substituted ketones via solvomercuration-oxidation (eqn 72). Peracids will also oxidize secondary alkylmercurials to ketones (eqn 73).[161]

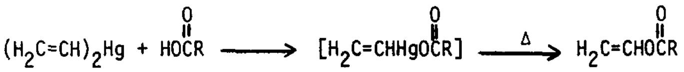


(72)



(73)

Oxidation can also be achieved via thermal decomposition of vinylmercuric salts. Treatment of divinylmercury with carboxylic acids affords the corresponding vinyl esters (eqn 74).[162–165] The more

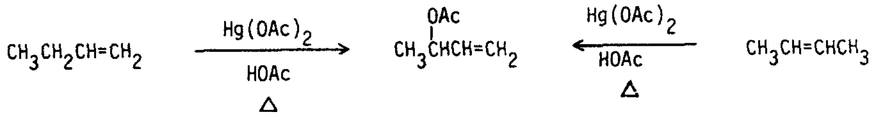


$$(H_2C{=}CH)_2Hg + HO\overset{O}{\overset{\|}{C}}R \longrightarrow [H_2C{=}CHHgO\overset{O}{\overset{\|}{C}}R] \xrightarrow{\Delta} H_2C{=}CHO\overset{O}{\overset{\|}{C}}R \tag{74}$$

acidic the carboxylic acid, the more readily does thermal decomposition of the vinylmercuric carboxylate occur. Unfortunately, this reaction is not stereospecific. Aryl vinyl ethers may be prepared in similar fashion (eqn 75).[162] Vinylsulfur and -phosphorous compounds have also been synthesized in this manner as will be discussed later.

$$(H_2C{=}CH)_2Hg + HOAr \xrightarrow{\Delta} \underset{73\text{-}100\%}{H_2C{=}CHOAr} \tag{75}$$

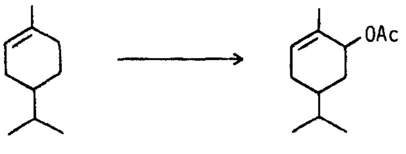
Many useful synthetic transformations of organomercurials proceed under solvolytic conditions. One reaction of considerable utility is the Treibs reaction, first reported in 1948.[166] Treatment of olefins with mercuric acetate usually in hot acetic acid generates allylic acetates directly (eqn 76). This reaction has proven quite useful for the preparation of allylic acetates due to the ease with which the reaction can be carried out, the convenient separation of the inorganic products, and the few side products observed. The following selected examples further illustrate its utility (eqns 77–79). Not all yields are as high as these, however, and isomeric mixtures are common, especially when unsymmetrical olefins are employed. Two side reactions occasionally observed are oxidation to enones or dehydrogenation to dienes, polyenes or arenes. The latter reaction has occasionally proven useful for the dehydrogenation of steroids. Mechanistically, the Treibs reaction appears to proceed via initial rate-determining allylmercuric acetate formation, followed by demercuration (eqn 80).[171,172] Allylmercurials are known to decompose regiospecifically in this fashion.



$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{HOAc}\ \Delta]{Hg(OAc)_2} CH_3\overset{\text{OAc}}{\overset{|}{C}}HCH{=}CH_2 \xleftarrow[\text{HOAc}\ \Delta]{Hg(OAc)_2} CH_3CH{=}CHCH_3 \qquad (76)$$

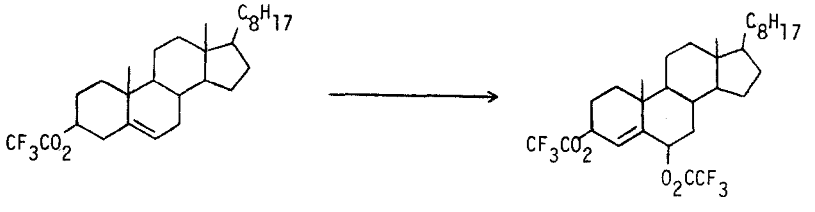
$$\underline{trans}\text{-}CH_3O_2C(CH_2)_6CH{=}CHCH_3 \longrightarrow \underline{trans}\text{-}CH_3O_2C(CH_2)_6CH{=}CHCH_2OAc \qquad (77)^{167}$$

85%



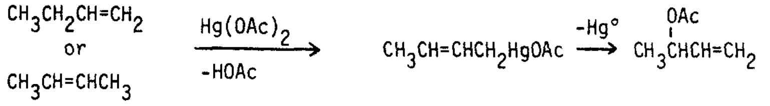
80%

(78)[168,169]



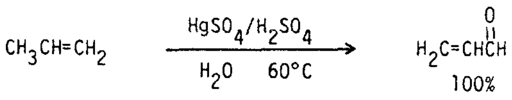
70%

(79)[170]



$$\begin{matrix} CH_3CH_2CH{=}CH_2 \\ \text{or} \\ CH_3CH{=}CHCH_3 \end{matrix} \xrightarrow[\text{-HOAc}]{Hg(OAc)_2} CH_3CH{=}CHCH_2HgOAc \xrightarrow{-Hg^\circ} CH_3\overset{\text{OAc}}{\overset{|}{C}}HCH{=}CH_2 \qquad (80)$$

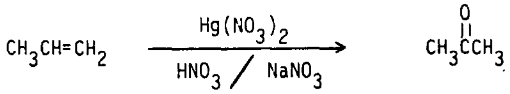
The oxidation of olefins to α,β-unsaturated carbonyl compounds becomes a major reaction when olefins are heated with a variety of mercurous and mercuric salts under aqueous conditions (eqn 81).[173] Although the reaction is fairly general and high yields are obtained, the reaction has never achieved industrial prominence due to difficulties in economically reoxidizing the mercury salts. Once again the reaction appears to proceed by solvolysis of an intermediate allylmercurial to an allylic alcohol, which is in turn oxidized to the ketone by the mercury salts.



$$CH_3CH{=}CH_2 \xrightarrow[H_2O\quad 60°C]{HgSO_4/H_2SO_4} H_2C{=}CH\overset{\text{O}}{\overset{\|}{C}}H \qquad (81)^{174}$$

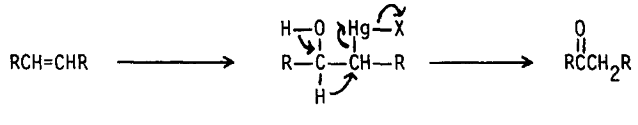
100%

Saturated carbonyl compounds can also be obtained from olefins under similar reaction conditions by simply using high concentrations of mercuric nitrate or by adding nitrous acid (eqn 82).[175,176] The



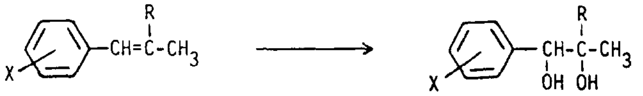
$$CH_3CH{=}CH_2 \xrightarrow[HNO_3\,/\,NaNO_3]{Hg(NO_3)_2} CH_3\overset{O}{\overset{\|}{C}}CH_3 \qquad (82)^{175}$$

solvolytic rearrangement of β-hydroxymercurials appears to be involved (eqn 83).[173]

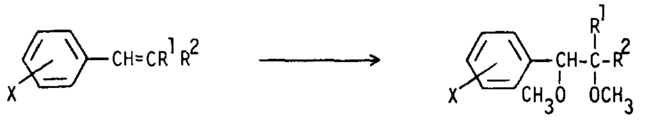


(83)

The solvomercuration of olefins is sometimes accompanied by rapid solvolysis of the intermediate organomercurial. Although few of these reactions appear general in scope, the oxy- or methoxymercuration of styrene and stilbene derivatives using highly electrophilic mercury salts results in direct diol or dimethyl ether formation (eqns 84, 85). Using arenes and mercury salts, one can also add either two

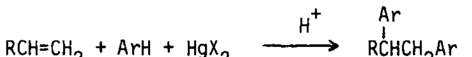


(84)[177,178]

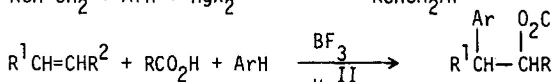


(85)[179,180]

aryl groups or an aryl group and a carboxylate group to the carbon–carbon double bond of simple olefins (eqns 86, 87). These reactions appear to proceed via carbomercuration of the double bond, followed by

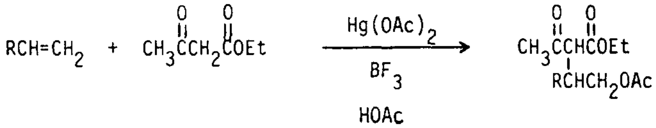


$$RCH{=}CH_2 + ArH + HgX_2 \xrightarrow{H^+} R\overset{Ar}{C}HCH_2Ar \qquad (86)^{181\text{-}183}$$



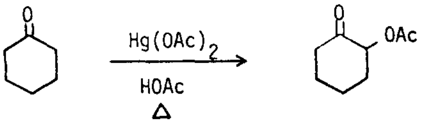
$$R^1CH{=}CHR^2 + RCO_2H + ArH \xrightarrow[Hg^{II}]{BF_3} R^1\overset{Ar}{C}H{-}\overset{O_2CR}{C}HR^2 \qquad (87)^{181,183,184}$$

solvolysis. β-Keto esters can be alkylated using similar conditions (eqn 88).[185]



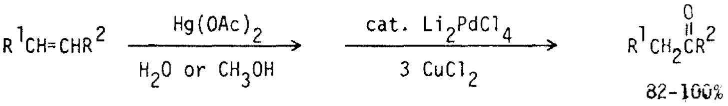
$$RCH{=}CH_2 + CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OEt \xrightarrow[BF_3\ \ HOAc]{Hg(OAc)_2} CH_3\overset{O}{\overset{\|}{C}}\underset{RCHCH_2OAc}{C}H\overset{O}{\overset{\|}{C}}OEt \qquad (88)$$

In his original publication on the reaction of olefins and mercuric acetate, Treibs also reported that ketones undergo acetoxylation upon heating with mercuric acetate in acetic acid (eqn 89).[166,186,187] Although this reaction appears somewhat limited in scope and the yields are frequently low, the reaction is quite regiospecific. For example, α-substituted ketones give only α′-substituted acetate products, and 3-methyl-[187] and 3,3-dimethylcyclohexanone[188] substitute only in the six position.



(89)

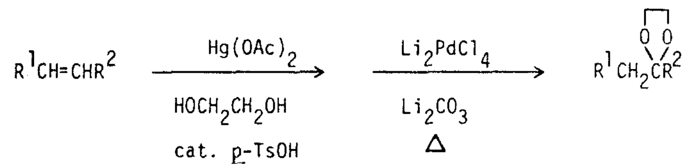
Organomercurials are also oxidized by a variety of metal salts. Reactions with palladium(II) salts have proven especially valuable. For example, solvomercuration–palladation of olefins provides a convenient route for the oxidation of olefins to ketones[189,190] or ketals[191] (eqns 90, 91).



$$R^1CH{=}CHR^2 \xrightarrow[H_2O\text{ or }CH_3OH]{Hg(OAc)_2} \xrightarrow[3\ CuCl_2]{cat.\ Li_2PdCl_4} R^1CH_2\overset{O}{\overset{\|}{C}}R^2$$

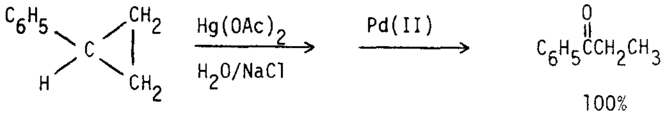
82-100%

(90)



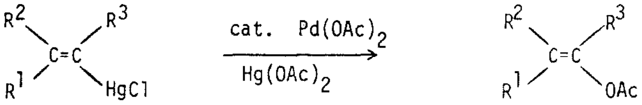
(91)

The oxymercuration–palladation of cyclopropanes also affords saturated ketones (eqn 92).[192]

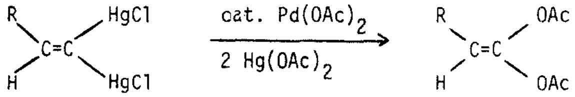


(92)

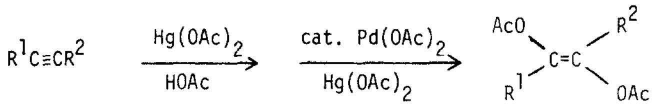
The treatment of vinylmercuric chlorides with palladium acetate provides a novel, stereospecific route to the corresponding enol acetates (eqn 93).[193] This reaction becomes catalytic in palladium when an equivalent of the corresponding mercuric carboxylate is added. By using other mercury(II) carboxylates a variety of enol esters can be prepared. Olefinic diacetates are also available in high yield if one employs dimercurials or β-acetoxymercurials (eqns 94, 95). The same overall transformation can also be effected by using lead tetraacetate although the yields are lower (eqn 96).



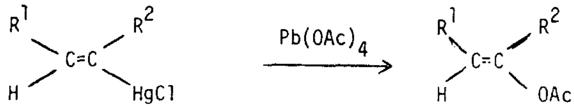
(93)



(94)

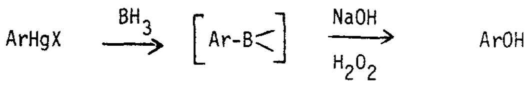


(95)



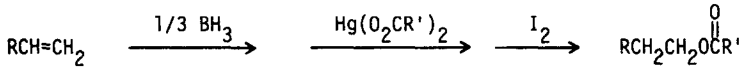
(96)

Finally, there are two organomercurial reactions involving organoboranes which possess synthetic utility. Treatment of arylmercuric halides or diarylmercurials with borane–THF generates intermediate arylboron compounds easily oxidized to phenols (eqn 97).[194] As briefly mentioned in Section 2, primary trialkylboranes derived from terminal olefins via hydroboration react readily with mercuric carboxylates



(97)

of weak acids, followed by iodine, to give excellent yields of alkyl esters (eqn 98).[128] This reaction proceeds through intermediate alkylmercurials to the corresponding iodides which are in turn rapidly esterified under the reaction conditions.



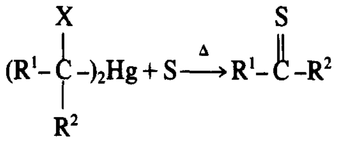
$$RCH{=}CH_2 \xrightarrow{1/3\ BH_3} \xrightarrow{Hg(O_2CR')_2} \xrightarrow{I_2} RCH_2CH_2O\overset{O}{\overset{\|}{C}}R' \qquad (98)$$

A wide variety of organosulfur compounds have also been synthesized from organomercury intermediates. For example, the direct reaction of arylmercurials and sulfur at elevated temperatures affords diaryl sulfides often in good yield (eqn 99).[195–199] At lower temperatures dialkyl and diaryl disulfides can be obtained (eqn 100).[200] Polyfluorinated dialkylmercury compounds give di- and polysulfides[201–203] at lower temperatures and perfluorothiocarbonyl compounds[203–205] at elevated temperatures (eqns 101, 102). In the presence of potassium or cesium fluoride, sulfur inserts into these same compounds at much lower temperatures to yield mercury(II) mercaptides readily converted into a variety of other sulfur compounds (eqn 103).[202,206,207]

$$Ar_2Hg + S \xrightarrow{220\text{–}250°} Ar_2S \qquad (99)$$

$$RHgCl + S \xrightarrow{140\text{–}180°} \underset{60\text{–}75\%}{R\text{-}S\text{-}S\text{-}R} \qquad (100)$$

$$R_2Hg + S \xrightarrow{200\text{–}250°} \underset{x = 2,3,4}{R\text{-}S_x\text{-}R} \qquad (101)$$

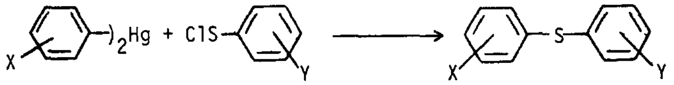


$$(R^1\text{-}\underset{R^2}{\overset{X}{C}}\text{-})_2Hg + S \xrightarrow{\Delta} R^1\text{-}\overset{S}{\overset{\|}{C}}\text{-}R^2 \qquad (102)$$

X = F, Cl 30–80%

$$R_2Hg + S \xrightarrow[\substack{70\text{–}100°\\ DMF}]{F^-} (RS)_2Hg \longrightarrow \underset{X = H,\ CH_3,\ SR,\ Cl}{RSX} \qquad (103)$$

Diaryl sulfides can also be prepared by reacting diarylmercurials with arylsulfenyl chlorides at room temperature (eqn 104).[208]



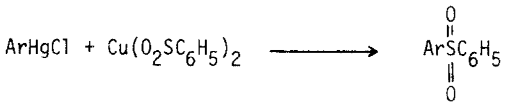
(104)

A wide variety of other organosulfur compounds have been prepared from organomercurials. Thiocyanogen reacts with both aryl-[209] and allylic[210] mercurials to afford the corresponding thiocyanates (eqn 105). Thiocyanates can also be obtained from arylmercurials upon treatment with cupric thiocyanate (eqn 106).[211] In like manner aryl sulfones can be prepared by using cupric benzenesulfinate (eqn

$$RHgX + (SCN)_2 \longrightarrow RSCN \qquad (105)$$

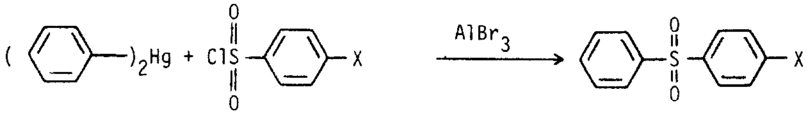
$$ArHgCl + Cu(SCN)_2 \longrightarrow ArSCN \qquad (106)$$

107).[211] Phenyl sulfones have also been obtained from the reaction of diphenylmercury and arylsulfonyl



$$ArHgCl + Cu(O_2SC_6H_5)_2 \longrightarrow ArS(=O)_2C_6H_5 \qquad (107)$$

chlorides in the presence of aluminum bromide (eqn 108).[212]



(108)

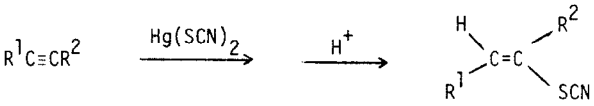
X=H, CH$_3$, Br

50-65%

Vinyl sulfur derivatives are also readily available from organomercurials by a variety of methods (eqns 109–112). Vinyl sulfides and sulfones can also be prepared in excellent yields by the photoinitiated reaction of vinylmercurials and disulfides or mercaptides, or benzenesulfonyl chloride or sulfinate salts respectively (eqns 113, 114).[217,218]

$$RSO_2Cl + (HC(=O)CH_2)_2Hg \longrightarrow R\text{-}S(=O)_2\text{-}O\text{-}CH{=}CH_2 \qquad (109)^{213}$$

$$SOCl_2 + (HC(=O)CH_2)_2Hg \longrightarrow O{=}S(O\text{-}CH{=}CH_2)_2 \qquad (110)^{213}$$

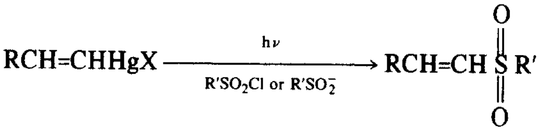


(111)[84]

$$H_2C{=}CHHgX \xrightarrow{\Delta} H_2C{=}CHX + Hg^\circ \qquad (112)$$

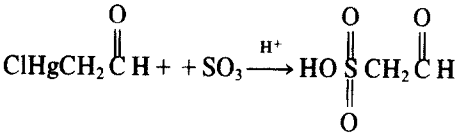
X=S$_2$COEt,[214] SCN,[214] SR,[162,163,215] SO$_2$Ar[162,216]

$$RCH{=}CHHgX \xrightarrow[R'SSR' \text{ or } R'S^-]{h\nu} RCH{=}CHSR' \qquad (113)$$



$$RCH{=}CHHgX \xrightarrow[R'SO_2Cl \text{ or } R'SO_2^-]{h\nu} RCH{=}CHS(=O)_2R' \qquad (114)$$

Sulfur dioxide or trioxide insert readily into the carbon–mercury bond of organomercurials. However, no sulfinic acid derivatives have ever been isolated from the sulfur dioxide adducts and few examples of sulfonic acids have been reported from the sulfur trioxide intermediates (eqn 115).[219]



$$ClHgCH_2C(=O)H + + SO_3 \xrightarrow{H^+} HOS(=O)_2CH_2C(=O)H \qquad (115)$$

While a wide variety of organosulfur compounds can be prepared from organomercurials, these reactions still have not been widely employed. One might expect this to change with the increasing visibility of organomercury chemistry. It should be noted that many of the methods employed in the preparation of organosulfur compounds are also applicable to the synthesis of organoselenium and -tellurium compounds.

A number of organic nitrogen compounds have also been synthesized from organomercury intermediates, although the majority of the work has concentrated on nitroso, nitro and diazonium compounds. For example, nitroso compounds are readily available from organomercurials and nitrosyl chloride (eqn 116). Nitrogen oxides react with arylmercurials to give either nitroso compounds or aryldiazonium salts or both, depending on the oxide used (N_2O_3 or N_2O_4), the arylmercurial and the manner in which the reaction is run (eqn 117).[223–226] Aryldiazonium salts are also obtained upon reacting arylmercurials with nitrosylsulfuric acid, or nitric acid plus sodium nitrite or nitrous oxide.[227–229]

$$R_2Hg + NOCl \longrightarrow R\text{-}NO \qquad (116)$$

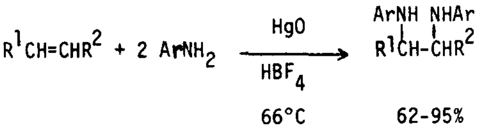
$$R = \text{polyhaloalkyl},^{220} \quad C{\equiv}CR',^{221} \quad Ar^{222,223}$$

$$Ar_2Hg \longrightarrow ArNO \text{ or } ArN_2^+ \qquad (117)$$

Aromatic nitro compounds are formed upon reacting arylmercurials and nitric acid (eqn 118).[223,230] Since this reaction proceeds with complete retention, this reaction may be of synthetic utility in those cases where the arylmercurial is readily available or direct nitration of the aromatic gives isomeric mixtures. Analogous reactions of arylmercurials and nitronium tetrafluoroborate (NO_2BF_4) produce complex mixtures of products and possess no synthetic utility.

$$ArHgX + HNO_3 \longrightarrow ArNO_2 \qquad (118)$$

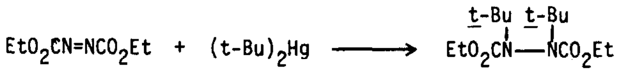
Several miscellaneous reactions involving organomercurials are worth noting. Vicinal diamines are available by treating olefins with arylamines and mercuric tetrafluoroborate (eqn 119).[231] Amino-mercuration and subsequent solvolysis are apparently involved. Dialkylation of the nitrogen–nitrogen double bond has been effected using di-*t*-butylmercury (eqn 120).[232] Urethanes are obtained upon reacting carboalkoxymercurials and amines (eqn 121).[233]



$$R^1CH{=}CHR^2 + 2\ ArNH_2 \xrightarrow[\text{HBF}_4]{\text{HgO}} R^1\overset{\text{ArNH}}{\overset{|}{C}}H\text{-}\overset{\text{NHAr}}{\overset{|}{C}}HR^2$$

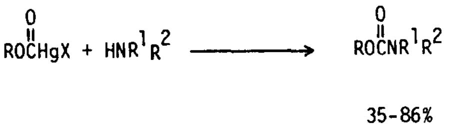
66°C 62-95%

(119)



$$EtO_2CN{=}NCO_2Et + (t\text{-}Bu)_2Hg \longrightarrow EtO_2C\overset{\underline{t}\text{-}Bu}{\overset{|}{N}}\text{—}\overset{\underline{t}\text{-}Bu}{\overset{|}{N}}CO_2Et$$

(120)

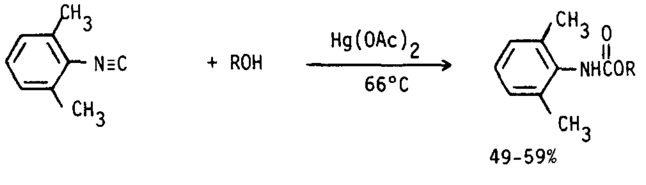


$$RO\overset{O}{\overset{\|}{C}}HgX + HNR^1R^2 \longrightarrow RO\overset{O}{\overset{\|}{C}}NR^1R^2$$

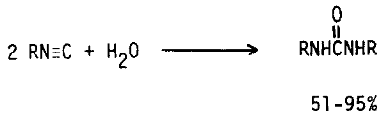
35-86%

(121)

Finally, a wide variety of nitrogen-containing compounds have been prepared by reacting isonitriles with mercury salts (eqns 122–128). It appears that all of these reactions involve intermediate imidoylmercurials.



(122)[234]



$$2\ RN{\equiv}C + H_2O \longrightarrow RNH\overset{\overset{O}{\|}}{C}NHR$$

51-95% (123)[234,235]

$$RN{\equiv}C + R^1R^2NH \longrightarrow RNH\overset{\overset{O}{\|}}{C}NR^1R^2$$

40-91% (124)[234-236]

$$RN{\equiv}C + \underline{n}\text{-}BuNH_2 \xrightarrow[66°C]{Hg(II)/NEt_3} \underline{n}\text{-}BuN{=}C{=}NR$$

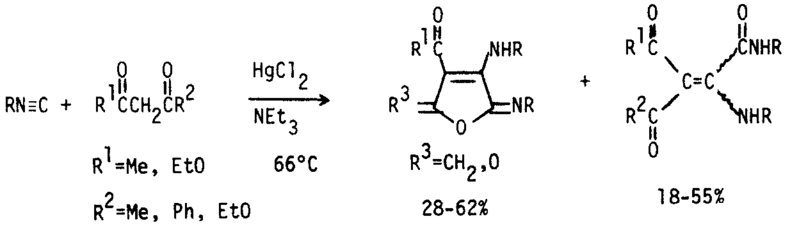
39-77% (125)[236]

$$RN{\equiv}C + R^1R^2NH \xrightarrow[66°C]{HgCl_2} RN{=}CHNR^1R^2$$

(126)[236]

$$RN{\equiv}C + R^1R^2NH \longrightarrow [RNH\overset{+}{C}(NR^1R^2)_2]Cl^-$$

39-98% (127)[234,236]



(128)[237]

A larger variety of phosphorus-containing compounds is available via organomercury intermediates than seen for nitrogen. Much of the work in this area was done very early on and other methods have since supplanted the organomercurial procedures. Thus, alkyl, vinyl and arylphosphines are obtained upon treating the appropriate organomercurials with phosphorus halides (eqns 129–132). The latter reaction has proven useful for the preparation of arylphosphine dichlorides not readily available by Friedel–Crafts procedures or for diarylphosphine chlorides where over-arylation is avoided.

$$R_2Hg + PCl_3 \xrightarrow{200\text{-}250°C} RPCl_2$$

R=alkyl (129)[238-240]

$$(H_2C{=}CH)_2Hg + PX_3 \xrightarrow{25\text{-}80°C} H_2C{=}CHPX_2$$

X=F, Cl, Br

30-78% (130)[241-243]

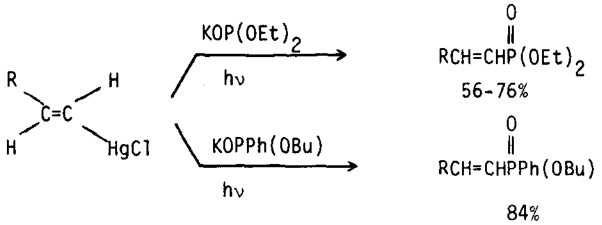
$$(RC{\equiv}CC{\equiv}C)_2Hg + PI_3 \longrightarrow (RC{\equiv}CC{\equiv}C)_3P$$

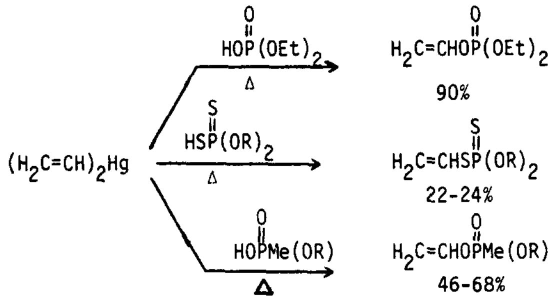
28-73% (131)[244]

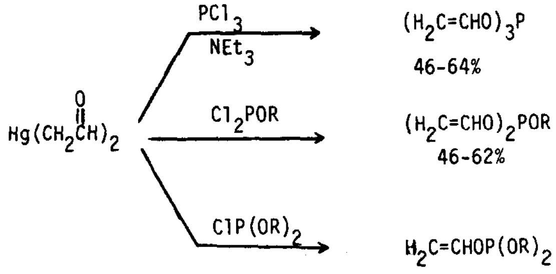
$$Ar_2Hg + RPCl_2 \longrightarrow Ar(R)PCl$$

R=Cl, Ar' (132)[245-248]

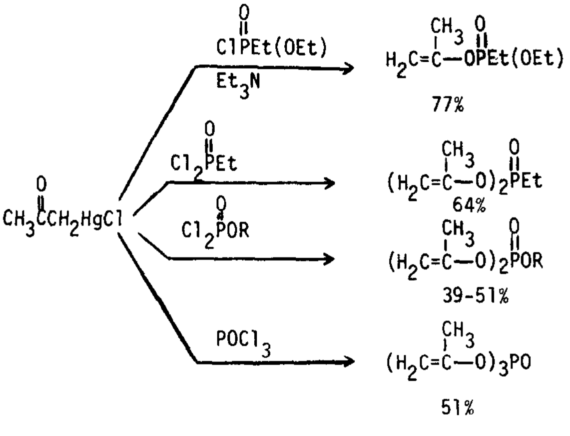
Organomercurials can be very useful intermediates for the preparation of a variety of vinyl phosphorus compounds (eqns 133, 134). Both types of reactions we have seen before. Unfortunately, some loss of stereochemistry is observed in the photostimulated reactions. Compounds similar to the latter phosphorus esters can also be obtained from α-halomercuricarbonyl compounds (eqn 135).[250]


(133)[217]


(134)[249]


(135)

Mercurated ketones work equally well in this type of reaction[251] and this concept can be extended to the synthesis of alkenylphosphorus compounds of all types (eqn 136).[252] In certain cases the phosphorus halides can be replaced by trialkylphosphites, or phosphorus(III) compounds containing phosphorus–hydrogen or phosphorus–metal bonds (eqns 137–140).

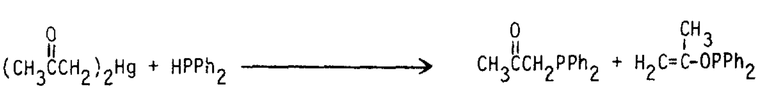

(136)

$$R\overset{O}{\overset{\|}{C}}CH_2HgX + P(OR')_3 \longrightarrow H_2C{=}\overset{R}{\overset{|}{C}}\text{-}O\overset{O}{\overset{\|}{P}}(OR')_2$$

(137)[253]

$$(R\overset{O}{\overset{\|}{C}}CH_2)_2Hg + HP(OBu)_2 \longrightarrow H_2C{=}\overset{R}{\overset{|}{C}}\text{-}OP(OBu)_2$$

(138)[254]



$$(CH_3\overset{O}{\overset{\|}{C}}CH_2)_2Hg + HPPh_2 \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2PPh_2 + H_2C{=}\overset{CH_3}{\overset{|}{C}}\text{-}OPPh_2$$

(139)[255,256]

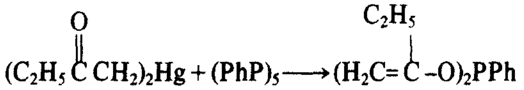
$$CH_3\overset{O}{\overset{\|}{C}}CH_2HgCl + KPPh_2 \longrightarrow H_2C{=}\overset{CH_3}{\overset{|}{C}}\text{-}OPPh_2$$

(140)[255,256]

When methyl- or phenylphosphine react with dibenzylmercury or α-mercurated carbonyl compounds, cyclic organophosphines are formed in high yield (eqn 141).[257,258]

$$RPH_2 + R_2'Hg \longrightarrow \underset{70\text{–}100\%}{(RP)_5} \qquad (141)$$

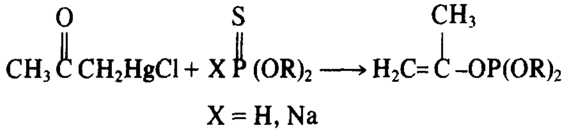
This provides one of the most convenient syntheses of this class of compounds. Further reaction with α-mercurated ketones has been reported to afford enol phosphorus compounds (eqn 142).[258]



$$(C_2H_5\overset{O}{\overset{\|}{C}}CH_2)_2Hg + (PhP)_5 \longrightarrow (H_2C{=}\overset{C_2H_5}{\overset{|}{C}}\text{-}O)_2PPh$$

(142)

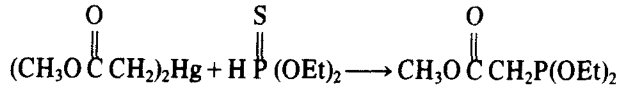
Finally, similar reactions of higher valent phosphorus compounds containing a phosphorus–sulfur bond are observed to occur with elimination of sulfur (eqns 143, 144).[259]



$$CH_3\overset{O}{\overset{\|}{C}}CH_2HgCl + X\overset{S}{\overset{\|}{P}}(OR)_2 \longrightarrow H_2C{=}\overset{CH_3}{\overset{|}{C}}\text{-}OP(OR)_2$$

$X = H, Na$

(143)



$$(CH_3O\overset{O}{\overset{\|}{C}}CH_2)_2Hg + H\overset{S}{\overset{\|}{P}}(OEt)_2 \longrightarrow CH_3O\overset{O}{\overset{\|}{C}}CH_2P(OEt)_2$$

(144)

As we have seen in this entire section, there are a multitude of ways in which organomercurials can be used in the synthesis of heteroatom-containing compounds. While many of these methods are very old and have been supplanted by newer, milder and/or more efficient approaches, there are still many other reactions here which should be of real interest to the synthetic organic chemist. In many cases the transformation involved is unique to organomercurials or provides a route unlike any other presently available.

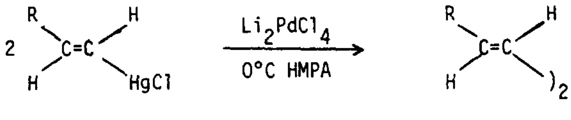
4. DIMERIZATION

The dimerization of organomercurials can be effected thermally, photolytically or more commonly by employing transition metal reagents. It provides a convenient entry into 1,3-dienes and biaryls, but has proven less useful for the synthesis of alkanes. The scope of these symmetrical dimerization reactions will be discussed in this section, while methods for unsymmetrical carbon–carbon bond formation will be deferred until Sections 5 and 6.

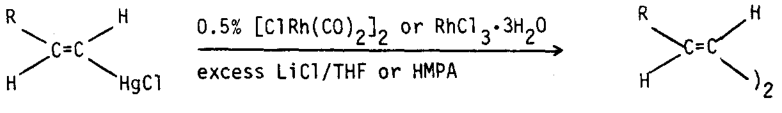
There do not appear to be any generally useful methods for the dimerization of alkylmercurials. Although there are scattered examples of the thermolysis or photolysis of simple alkylmercurials giving dimerization, free radicals are usually generated and yields of dimer are generally quite low. Benzyl-mercurials are more easily dimerized by thermolysis,[260] photolysis[261] or transition metal promoted dimerization.[262]

Vinylmercurials are readily dimerized to 1,3-dienes using a variety of procedures. Both palladium(O)[263,264] and palladium(II)[264] reagents effect dimerization (eqns 145, 146). While the former reagent is catalytic, some loss of stereochemistry is observed. The latter approach is highly stereospecific, but requires stoichiometric amounts of palladium and a carcinogenic solvent. Fortunately, these difficulties are overcome by using rhodium reagents (eqn 147).[265] Slightly better yields are obtained using the rhodium(I) catalyst, but low yields are observed for more hindered vinylmercurials. All of these reactions apparently proceed via intermediate vinylpalladium or vinylrhodium intermediates.

$$(RCH{=}CH)_2Hg \xrightarrow[CH_3CN\text{ or }CH_3OH]{\text{cat. }Pd(PPh_3)_4} (RCH{=}CH)_2 \tag{145}$$



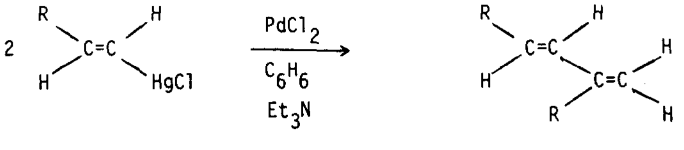
(146)



(147)

92-100%

More recently it has been noted that the palladium reactions are highly solvent dependent. By switching from a highly polar solvent such as HMPA which is required to get high yields of symmetrical dimers to a non-polar solvent such as benzene, one can completely reverse the mode of cross-coupling and isolate excellent yields of "head-to-tail" dimers (eqn 148).[266] Unlike the results in HMPA, this reaction can be made catalytic in palladium by adding two equivalents of anhydrous cupric chloride.



(148)

88-98%

Arylmercurials can also be readily dimerized to biaryls by a number of procedures. Although electron-rich arenes are oxidatively dimerized by mercuric trifluoroacetate plus boron trifluoride etherate (eqn 149),[267] this reaction probably does not involve intermediate arylmercurials, but more likely electron transfer processes. Thallium trifluoroacetate, lead tetraacetate and cobalt trifluoride give superior yields.

$$2\ ArH \xrightarrow[BF_3\cdot Et_2O]{Hg(O_2CCF_3)_2} Ar{-}Ar \tag{149}$$

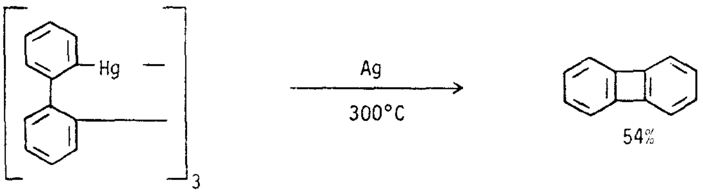
Transition metals are once again very effective in the dimerization of arylmercurials. Wilkinson's catalyst, $ClRh(PPh_3)_3$, in HMPA quantitatively dimerizes diphenylmercury to biphenyl.[268] Catalytic amounts of $[ClRh(CO)_2]_2$ also very effectively dimerize arylmercuric chlorides under conditions almost identical to those used to effect the dimerization of vinylmercuric chlorides (eqn 150).[265]

$$2\ ArHgCl \xrightarrow[\substack{4\ LiCl\quad HMPA\\ 80^\circ\quad 24\,hr}]{0.5\%\ [ClRh(CO)_2]_2} \underset{40\text{–}96\%}{Ar{-}Ar} \tag{150}$$

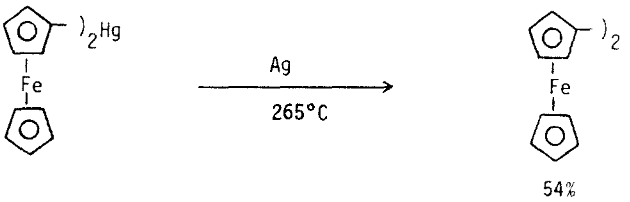
Dilithium tetrachloropalladate also readily dimerizes phenylmercuric salts, diphenylmercury and ferrocenylmercurials.[264,269] This reaction becomes catalytic when cupric chloride or copper powder are added to the reaction.[270,271] Heating arylmercuric halides with copper powder and catalytic amounts of palladium chloride in pyridine is also a highly effective route to biaryls (eqn 151).[271] The above rhodium and palladium procedures nicely complement the classical reaction. The $[ClRh(CO)_2]_2$ procedure tolerates phenols.[265] The $PdCl_2/CuCl_2$ procedure apparently accommodates carboxylic acid groups,[270] and the $PdCl_2/Cu$ system works well with amine-containing arylmercurials. Biaryls can also be prepared directly from arenes upon treatment with mercuric acetate and palladium acetate, but this approach gives almost all possible regioisomers in the dimerization of toluene.[272]

$$2\ ArHgX \xrightarrow[C_5H_5N \quad 115^\circ]{\text{cat. } PdCl_2/Cu} \underset{47\text{–}95\%}{Ar\text{–}Ar} \qquad (151)$$

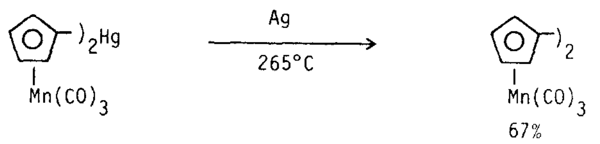
Arylmercurials have also frequently been dimerized by the use of silver at elevated temperatures. Although the yields are not always high, there are several interesting examples of this reaction (eqns 152–154).



(152)[273]



(153)[274]



(154)[275]

As we have seen, a number of effective methods are available for the dimerization of benzylic, vinyl- and arylmercurials. However, no good procedure presently exists for the dimerization of alkylmercurials.

5. ALKYLATION

The direct substitution of mercury in organomercurials by carbon is a reaction of considerable synthetic importance. Unfortunately, to date methods for the alkylation of organomercurials are limited to a few examples of reactions with organic halides and several rather limited organometallic cross-coupling procedures.

The most obvious approach to the alkylation of organomercurials, the reaction with organic halides (eqn 155), is quite restricted. Almost all successful examples of this reaction have been achieved using triphenylmethyl halides or related benzylic halides. Cross-coupling has been observed with alkyl-,[276–280]

$$R_2Hg + R'X \longrightarrow R\text{–}R' + RHgX \qquad (155)$$

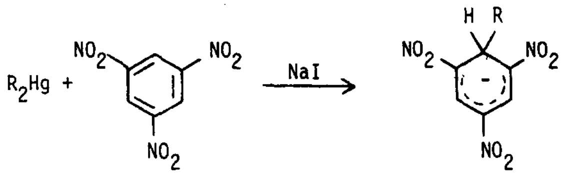
benzylic,[281,282] aryl-,[279,280,282–286] ferrocenyl,[287] vinyl[282,288] and a wide variety of α-mercurated carbonyl compounds.[64,65,280,289–292] Few other successful alkylations have been reported. Chemically induced dynamic nuclear polarization (CIDNP) experiments suggest that many of these reactions may be proceeding via radical intermediates.[278,281,288] A common side reaction with alkylmercurials is beta hydride abstraction (eqn 156).[276,277] In the reaction of α-mercurated carbonyl compounds alkylation occurs either on carbon or on oxygen depending on the electronic nature of the organic halide,[289] the solvent[280,290,291] and the substituents present in the organomercurial.[290]

$$RCH_2CH_2HgX + Ph_3CX \longrightarrow RCH{=}CH_2 + Ph_3CH + HgX_2 \qquad (156)$$

The effect of added Lewis acids on these alkylations has also been studied. While some reactions have been promoted by such additions, others are actually inhibited. Although aluminum bromide does promote the alkylation of diphenyl- and dibenzylmercury, the yields are still too low to be of real synthetic interest (eqn 157).[212]

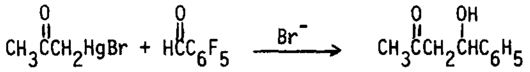
$$R_2Hg + R'X \xrightarrow[CH_2Cl_2]{AlBr_3} \underset{20\text{–}60\%}{R\text{–}R'} \qquad (157)$$

An alternate approach to the alkylation of organomercurials takes advantage of the increased nucleophilicity of the organic groups attached to mercury when halide anions are present (eqns 158–160).

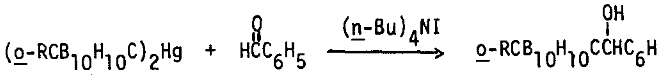


(158)[282,293,294]

$R = CN,\ CCl_3,\ CH(CF_3)_2,\ C_6F_5,\ C{\equiv}CPh,\ CH_2\overset{O}{\overset{\|}{C}}CH_3,\ EtO_2CCHPh,$ o-carboranyl

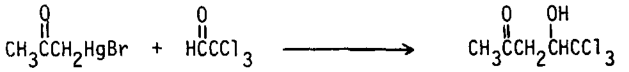


$$CH_3\overset{O}{\overset{\|}{C}}CH_2HgBr + H\overset{O}{\overset{\|}{C}}C_6F_5 \xrightarrow{Br^-} CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{OH}{\overset{|}{C}}HC_6H_5 \qquad (159)^{295}$$



$$(o\text{-}RCB_{10}H_{10}C)_2Hg + H\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{(n\text{-}Bu)_4NI} o\text{-}RCB_{10}H_{10}C\overset{OH}{\overset{|}{C}}HC_6H_5 \qquad (160)^{296}$$

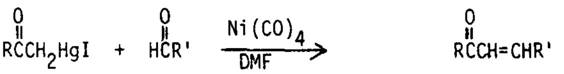
Apparently halides are not always necessary however (eqns 161, 162). A type of directed aldol condensation has also been reported using α-mercurated carbonyl compounds, aldehydes and nickel



$$CH_3\overset{O}{\overset{\|}{C}}CH_2HgBr + H\overset{O}{\overset{\|}{C}}CCl_3 \longrightarrow \underset{60\%}{CH_3\overset{O}{\overset{\|}{C}}CH_2\overset{OH}{\overset{|}{C}}HCCl_3} \qquad (161)^{295}$$

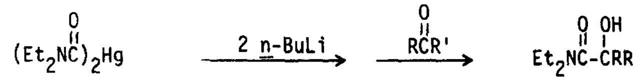
$$[(NO_2)_3C]_2Hg + H_2CO \longrightarrow \underset{82\%}{(NO_2)_3CCH_2OH} \qquad (162)^{297}$$

tetracarbonyl (eqn 163).[298] Carboxamidomercurials when first reacted with n-butyl lithium can also be



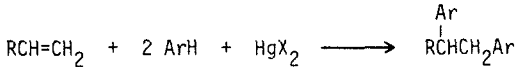
$$R\overset{O}{\overset{\|}{C}}CH_2HgI + H\overset{O}{\overset{\|}{C}}R' \xrightarrow[DMF]{Ni(CO)_4} \underset{\sim 70\text{-}90\%}{R\overset{O}{\overset{\|}{C}}CH{=}CHR'} \qquad (163)$$

added to carbonyl groups (eqn 164).[299] Methyl iodide, benzoyl chloride and ethyl benzoate also react with this reagent to afford Et_2NCOCH_3 (23%) and $Et_2NCOCOC_6H_5$ (65% and 31%) respectively.

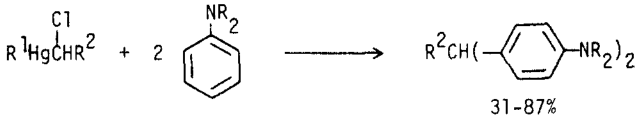


$$(Et_2N\overset{O}{\overset{\|}{C}})_2Hg \xrightarrow{2\ n\text{-}BuLi} \xrightarrow{R\overset{O}{\overset{\|}{C}}R'} Et_2N\overset{O}{\overset{\|}{C}}\text{-}\overset{OH}{\overset{|}{C}}RR' \qquad (164)$$

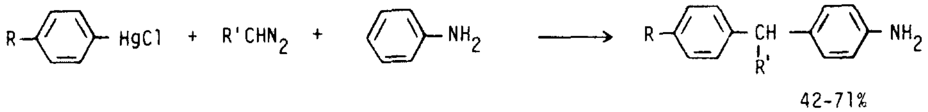
In all the above reactions, the organic group in the organomercurial has functioned as a nucleophile. There are several examples in the literature in which the organomercurial apparently reacts as an electrophile in carbon–carbon bond forming reactions (eqns 165–168). There are also two cases in which nucleophiles have been shown to directly displace the mercury moiety in organomercurials (eqns 169, 170). This latter reaction apparently proceeds by a photostimulated free radical chain process ($S_{RN}1$).



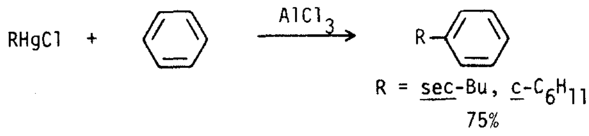
$$RCH{=}CH_2 + 2\,ArH + HgX_2 \longrightarrow RCH(Ar)CH_2Ar \qquad (165)^{181-183}$$



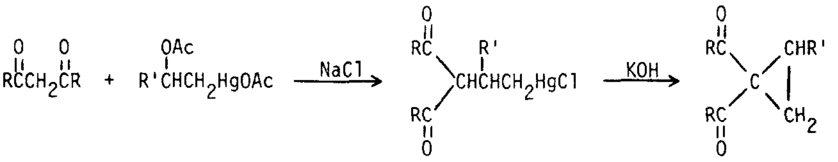
(166)[300,301]



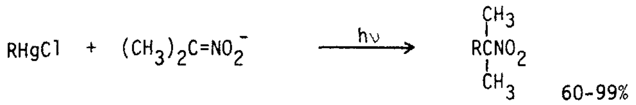
(167)[300]



(168)[302,303]

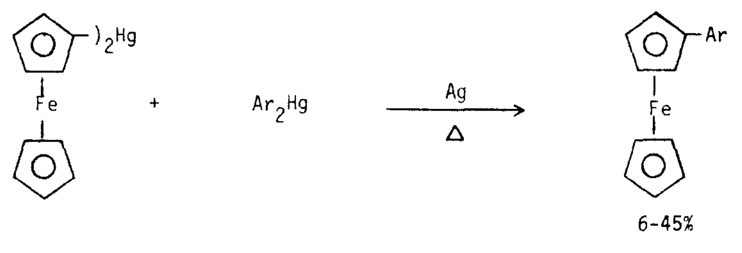


(169)[304,305]



$$RHgCl + (CH_3)_2C{=}NO_2^- \xrightarrow{h\nu} RC(CH_3)_2NO_2 \quad 60\text{-}99\% \qquad (170)^{306}$$

Several organometallic procedures have been reported to effect carbon–carbon bond formation via organomercurials. For example, the silver promoted dimerization of organomercurials discussed in the last section has been utilized to effect the cross-coupling of organomercurials as well (eqn 171).[274] The yields are quite low however.

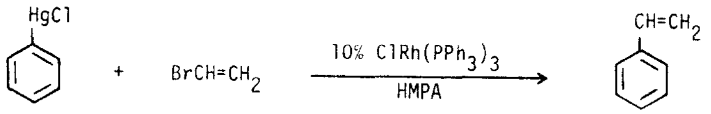


(171)

Organorhodium intermediates can be employed to effect the methylation of vinyl-, alkynyl- and arylmercurials (eqn 172).[307] While this approach appears limited to the methylation of organomercurials

$$RHgCl + CH_3RhI_2(PPh_3)_2 \xrightarrow[HMPA]{\Delta} \underset{91\text{-}99\%}{R\text{-}CH_3} \qquad (172)$$

and it requires stoichiometric amounts of expensive rhodium, it appears that this concept can be extended to the catalytic cross-coupling of certain organomercurials and organic halides (eqn 173).



(173)

Copper reagents appear to be more useful for the alkylation of a wide variety of organomercurials (eqns 174, 175). Secondary alkylmercuric bromides can be cross-coupled with *t*-butyl lithium by adding (*n*-Bu)$_3$P·CuI and oxidizing with nitrobenzene (eqn 176).[310] The complex organometallic suggested for these reactions will also react with primary alkyl iodides to give cross-coupling products (eqn 177). We have recently observed that this type of cross-coupling reaction can be effected in good yield using a wide variety of organomercurials and simple organocuprate reagents (eqns 178–180).[311] This reaction accommodates certain functional groups, proceeds in greater than 99% stereospecificity with vinylmercurials, and can be used in conjunction with oxymercuration to add the elements of OH and CH$_3$ across the carbon–carbon double bond of an olefin. At present it appears to be the most general method for the alkylation of a wide range of organomercurials.

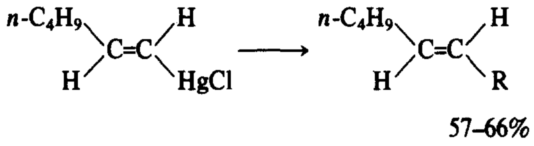
$$(PhC{\equiv}C)_2Hg + PhC{\equiv}CBr \xrightarrow{CuBr} \underset{100\%}{(PhC{\equiv}C)_2} \qquad (174)^{308}$$

$$(CF_3)_2Hg + ArI \xrightarrow{Cu} \underset{65\text{–}88\%}{Ar\text{–}CF_3} \qquad (175)^{309}$$

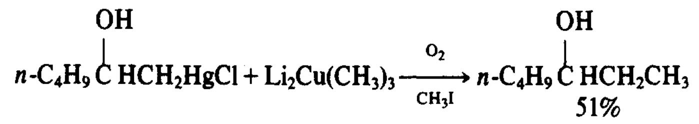
$$RHgBr \xrightarrow[-78^\circ]{(n\text{-}Bu)_3P\cdot CuI} \xrightarrow{3t\text{-}BuLi} \xrightarrow{C_6H_5NO_2} \underset{40\text{–}75\%}{R\text{–}C(CH_3)_3} \qquad (176)$$

$$RHgBr \xrightarrow{(n\text{-}Bu)_3P\cdot CuI} \xrightarrow{t\text{-}BuLi} \xrightarrow{R'I} \underset{21\text{–}70\%}{R\text{–}R'} \qquad (177)$$

$$\begin{array}{l} ArHgCl + Li_nCuR_{n+1} \xrightarrow[(RI)]{O_2} Ar\text{–}R \\ \quad n = 1,2 \qquad\qquad\quad 35\text{–}92\% \end{array} \qquad (178)$$



(179)

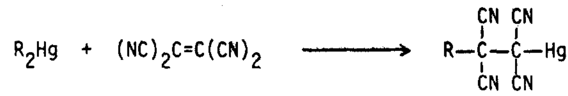


$$n\text{-}C_4H_9\overset{OH}{\overset{|}{C}}HCH_2HgCl + Li_2Cu(CH_3)_3 \xrightarrow[CH_3I]{O_2} n\text{-}C_4H_9\overset{OH}{\overset{|}{C}}HCH_2CH_3 \quad 51\% \qquad (180)$$

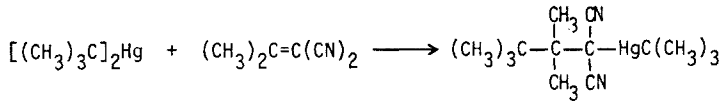
6. ALKENE AND ALKYNE ADDITION AND SUBSTITUTION REACTIONS

While few organomercurials will add directly to carbon–carbon double or triple bonds or to substitute olefinic or acetylenic hydrogens, such reactions can be effected via generation of free radicals or organopalladium compounds readily available from organomercurials. These reactions nicely supplement the limited number of approaches available for the alkylation of organomercurials.

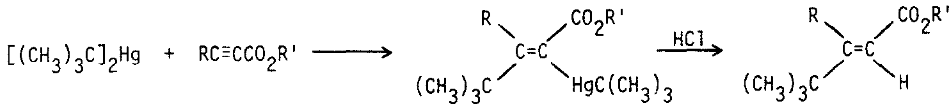
There are few examples of the direct addition of organomercurials to carbon–carbon double or triple bonds. Primary, secondary and benzylic dialkylmercurials will add to tetracyanoethylene[312–314] and di-*t*-butylmercury adds stereo- and regioselectively to a variety of electron deficient olefins and acetylenes, as well as diethyl azodicarboxylate[232] (eqns 181–184). The third reaction provides an interesting stereospecific trisubstituted olefin synthesis.



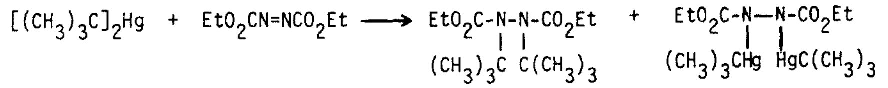
$$R_2Hg + (NC)_2C{=}C(CN)_2 \longrightarrow R\text{–}\underset{CN}{\overset{CN}{C}}\text{–}\underset{CN}{\overset{CN}{C}}\text{–}HgR \qquad (181)$$



$$[(CH_3)_3C]_2Hg + (CH_3)_2C{=}C(CN)_2 \longrightarrow (CH_3)_3C-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CN}{\overset{CN}{C}}-HgC(CH_3)_3 \qquad (182)$$



(183)



$$[(CH_3)_3C]_2Hg + EtO_2CN{=}NCO_2Et \longrightarrow EtO_2C-\underset{(CH_3)_3C}{N}-\underset{C(CH_3)_3}{N}-CO_2Et + EtO_2C-\underset{(CH_3)_3CHg}{N}-\underset{HgC(CH_3)_3}{N}-CO_2Et \qquad (184)$$

Recently, a wide variety of electron deficient olefins have been alkylated by generating free radicals from the reaction of alkylmercurials and $NaBH_4$ or $NaHB(OCH_3)_3$ (eqn 185).[315-325] A variety of solvents have been employed. The olefin is usually used in excess and good yields are obtained based on organomercurial. Primary, secondary and tertiary alkyl- and benzylic mercurials have been employed, as well as those derived from olefins and cyclopropanes via methoxymercuration. The nature of the alkyl group seems to be much less important than the nature of the alkene. The relative reactivities of a variety of olefins have been determined.[324] In general, the less sterically hindered the double bond is and the stronger the electron withdrawing group(s) attached to the double bond, the higher the yield. Terminal olefins give significantly better results than internal olefins. The following mechanism has been suggested for this reaction (eqns 186–189). This reaction has been used to study the selectivity of alkyl radicals towards various olefins as a function of temperature.[324]

$$RHgX + R^1CH{=}CR^2R^3 \xrightarrow[NaHB(OCH_3)_3]{NaBH_4\ or} RR^1CHCHR^2R^3 \qquad (185)$$

$$RHgX + NaBH_4 \longrightarrow RHgH \qquad (186)$$

$$RHgH \longrightarrow R\cdot + Hg^\circ + H\cdot \qquad (187)$$

$$R\cdot + H_2C{=}CHX \longrightarrow RCH_2\dot{C}HX \qquad (188)$$

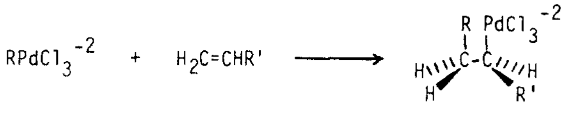
$$RCH_2\dot{C}HX + RHgH \longrightarrow RCH_2CH_2X + Hg^\circ + R\cdot \qquad (189)$$

This alkene addition reaction is nicely complemented by a reaction first reported in 1968 by R. F. Heck in which vinyl hydrogen substitution is effected by treating olefins with organomercurials and

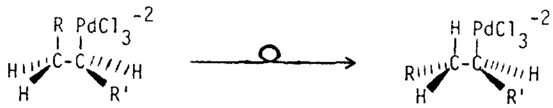
$$RHgCl + H_2C = CHR' \xrightarrow{Li_2PdCl_4} RCH{=}CHR' \qquad (190)$$

palladium(II) salts (eqn 190).[326] This reaction is believed to proceed as follows (eqns 191–195):[327,328]

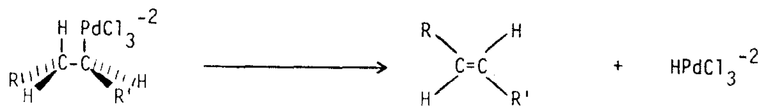
$$RHgCl + PdCl_4^{-2} \longrightarrow RPdCl_3^{-2} + HgCl_2 \qquad (191)$$



(192)



(193)



(194)

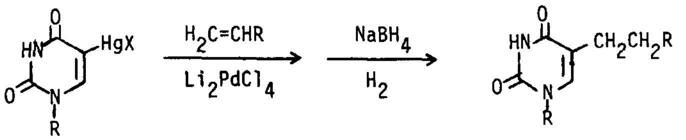
$$HPdCl_3^{-2} \longrightarrow HCl + Pd^{\circ} + 2\ Cl^{-} \qquad (195)$$

The intermediacy of organopalladium compounds has been established by actually isolating such compounds in some cases or by observing their dimerization or carbonylation products. Cis olefin insertion products have also been isolated when certain cyclic olefins or dienes are employed in this reaction. Addition occurs so as to place the organic moiety on the less hindered end of the original double bond. Steric rather than electronic factors seem to predominate. After olefin insertion, a new organopalladium intermediate is formed bearing beta hydrogen atoms. Such compounds are known to be quite unstable and to rapidly eliminate in a cis manner the elements of $HPdCl_3^{-2}$ which in turn decomposes to hydrochloric acid and palladium metal. For obvious reasons, the initial organomercurial cannot possess an alkyl group bearing beta hydrogens.[329] In those cases where more than one cis beta hydrogen is available, mixtures of isomers are common.

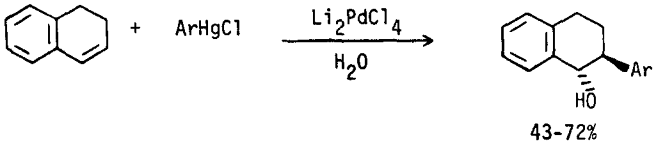
A large number of examples of the Heck reaction have been reported and a number of generalizations can be made. It can be run at room temperature in air in a variety of solvents. Methyl, benzyl, neopentyl, neophyl, carboalkoxy, simple aryl, polynuclear aromatic, heterocyclic and organometallic organomercurials can be employed. Neither alkylmercurials bearing beta hydrogens nor vinylmercurials are accommodated. Arylmercurials bearing electron withdrawing groups give substantially higher yields than those with electron donating groups.[326] A wide range of functional groups can also be incorporated into either the organomercurial or the olefin. However, allylic alcohols, esters and halides as well as enol esters give entirely different products as we will see. In the olefin, electron withdrawing groups increase the rate of reaction and generally the yield. The less hindered the double bond is, the more reactive it will be.

One of the major disadvantages of the Heck reaction using organomercurials is that it requires stoichiometric amounts of the palladium(II) salts, since palladium(II) is reduced to elemental palladium during the course of the reaction. Palladium reoxidants can be employed, but yields are generally not very good. The initial organopalladium species can also be generated by oxidative addition of organic halides to palladium(O), in which case the reaction can be made catalytic in palladium, but higher temperatures are required, yields are generally no higher, and mixtures of isomers are common.

These organopalladium reactions can also be used to alkylate olefins. For example, olefination followed by hydrogenation provides an overall alkylation process (eqn 196).[330] When the arylation of aryl olefins is carried out under aqueous conditions hydroxyarylation is effected (eqn 197).[331] This reaction

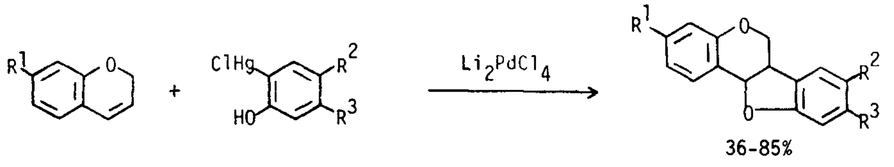


(196)

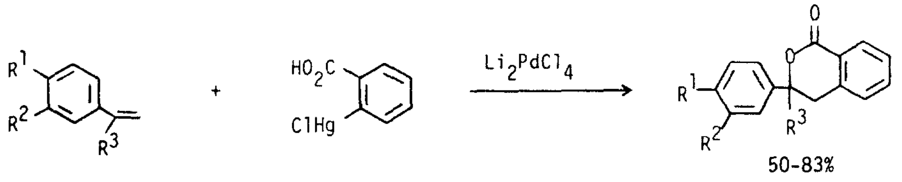


(197)

has been applied to the novel synthesis of several important naturally occurring ring systems (eqns 198, 199). Under strongly acidic phase transfer conditions, conjugate addition to enones can actually be

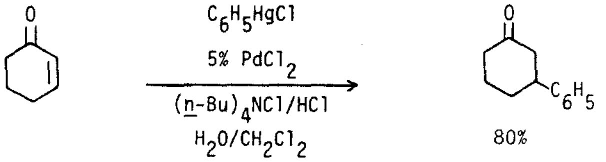


(198)[332]



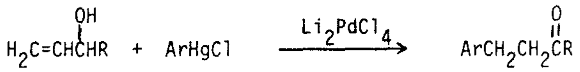
(199)[333]

effected catalytically in palladium in high yield (eqn 200).[334]



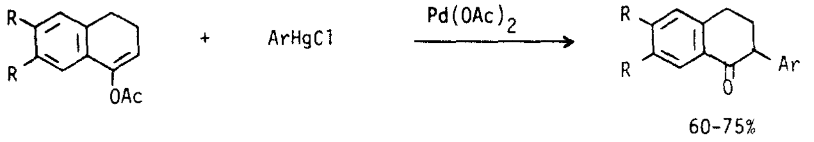
(200)

While many functional groups are accommodated by the Heck reaction, certain groups change the nature of the reaction completely. For example, primary and secondary allylic alcohols afford low yields of β-substituted carbonyl compounds (eqn 201).[335] Palladium hydride elimination obviously is directed towards the hydroxy group generating an enol of the eventual carbonyl product.



$$H_2C{=}CH\overset{OH}{C}HR + ArHgCl \xrightarrow{Li_2PdCl_4} ArCH_2CH_2\overset{O}{\overset{\|}{C}}R \qquad (201)$$

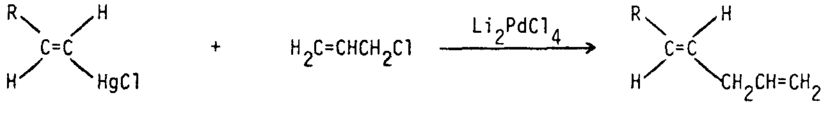
Although many enol esters react in the normal fashion with organopalladium compounds, there is one notable exception which has proven very useful for the synthesis of isoflavanones (eqn 202).[336] The ketone is obtained directly in the reaction, not after an hydrolysis step. Similar carbonyl products are frequently observed as side products in the reactions of enol esters.



(202)

The reaction of allylic acetates and halides generally produces allylation products (eqns 203, 204). Although the yields are not always high, the reaction is applicable to both aryl- and vinylmercurials and

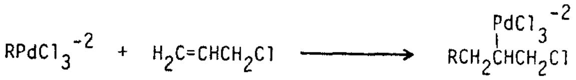
$$ArHgCl + H_2C{=}CHCH_2Cl \xrightarrow[(CuCl_2)]{cat.\ LiPdCl_3} ArCH_2CH{=}CH_2 \qquad (203)^{337}$$



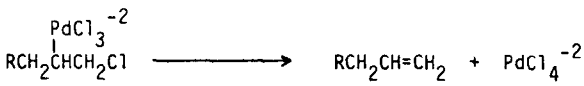
(204)[338]

proceeds catalytically in palladium even without added reoxidants. As in other organopalladium reactions with olefins, the yields drop sharply with increasing substitution about the olefin double bond. The suggested mechanism for this reaction follows (eqns 205–207). As the mechanism indicates, substitution occurs in an S_N2' fashion.

$$RHgCl + PdCl_4^{-2} \longrightarrow RPdCl_3^{-2} + HgCl_2 \qquad (205)$$

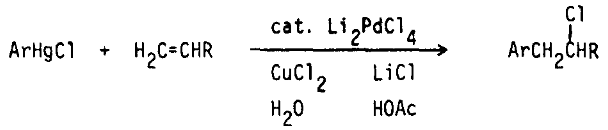


$$RPdCl_3^{-2} + H_2C{=}CHCH_2Cl \longrightarrow RCH_2\overset{PdCl_3^{-2}}{\overset{|}{C}}HCH_2Cl \qquad (206)$$



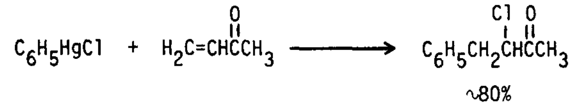
$$\mathrm{RCH_2\overset{PdCl_3^{-2}}{C}HCH_2Cl} \longrightarrow \mathrm{RCH_2CH{=}CH_2} + \mathrm{PdCl_4^{-2}} \qquad (207)$$

When the Heck reaction is carried out in the presence of high concentrations of cupric chloride, still another type of product is observed (eqn 208).[339] This reaction provides a useful method for the



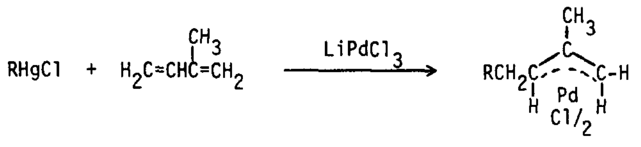
$$\mathrm{ArHgCl} + \mathrm{H_2C{=}CHR} \xrightarrow[\substack{\mathrm{CuCl_2} \quad \mathrm{LiCl} \\ \mathrm{H_2O} \quad \mathrm{HOAc}}]{\text{cat. } \mathrm{Li_2PdCl_4}} \mathrm{ArCH_2\overset{Cl}{C}HR} \qquad (208)$$

chloroarylation of olefins and works nicely for the synthesis of α-chloro carbonyl compounds (eqn 209).



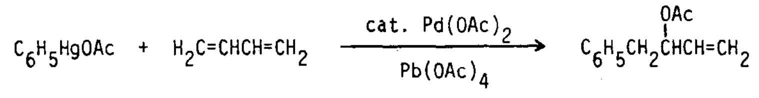
$$\mathrm{C_6H_5HgCl} + \mathrm{H_2C{=}CH\overset{O}{\overset{\|}{C}}CH_3} \longrightarrow \underset{\sim 80\%}{\mathrm{C_6H_5CH_2\overset{Cl}{C}H\overset{O}{\overset{\|}{C}}CH_3}} \qquad (209)$$

Heck type reactions also afford a valuable route to π-allylpalladium compounds which have found considerable application in organic synthesis of late. For example, organopalladium additions to 1,3-dienes afford modest yields of π-allylpalladium compounds (eqn 210).[340,341] By employing only



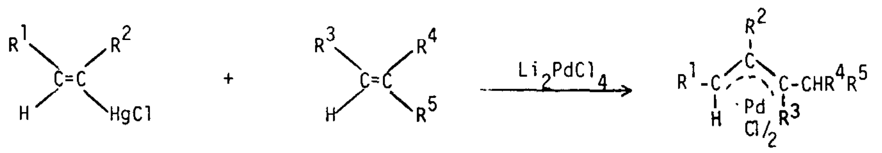
(210)

catalytic amounts of palladium acetate and an equivalent of lead tetraacetate in this reaction, allylic acetates can be isolated instead (eqn 211).[340] The reaction of vinylmercurials, $\mathrm{Li_2PdCl_4}$ and simple olefins



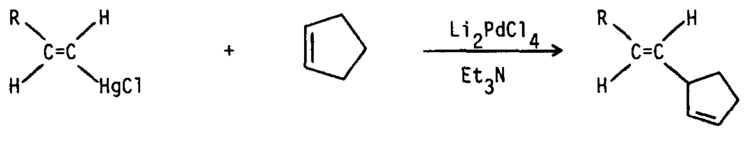
$$\mathrm{C_6H_5HgOAc} + \mathrm{H_2C{=}CHCH{=}CH_2} \xrightarrow[\mathrm{Pb(OAc)_4}]{\text{cat. } \mathrm{Pd(OAc)_2}} \mathrm{C_6H_5CH_2\overset{OAc}{C}HCH{=}CH_2} \qquad (211)$$

also affords π-allylpalladium compounds (eqn 212).[342] Both acyclic and monocyclic olefins can be

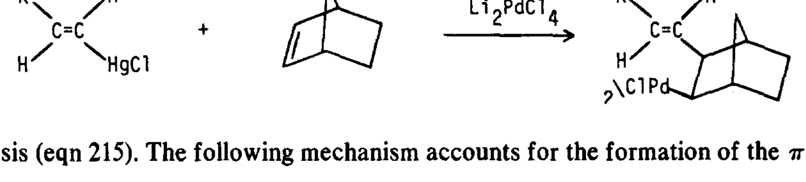


(212)

employed in this reaction. When cyclic olefins are used and triethylamine added, one obtains 1,4-dienes instead (eqn 213).[343] With bicyclic olefins such as norbornene, stable, sigma bonded alkylpalladium compounds can be isolated in high yield (eqn 214).[344] These compounds are versatile intermediates in

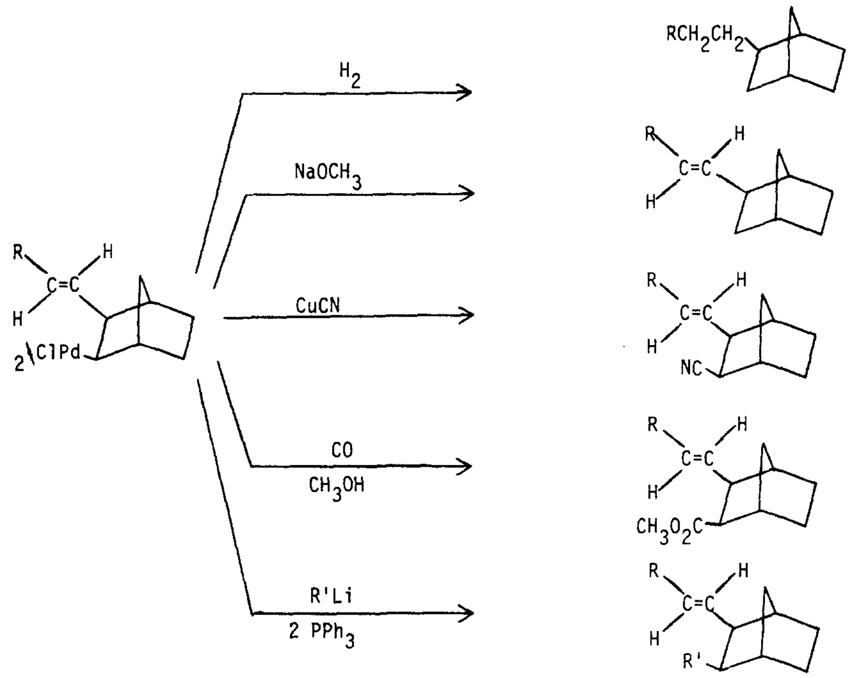


(213)



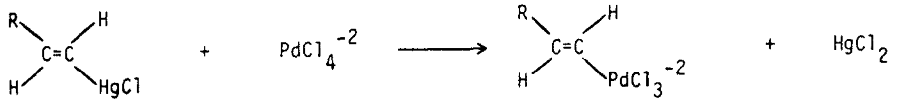
(214)

organic synthesis (eqn 215). The following mechanism accounts for the formation of the π-allylpalladium

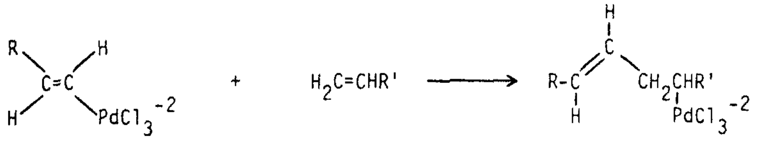


(215)

compounds (eqns 216–219). It should be noted that a number of other stable alkylpalladium compounds have been obtained from organopalladium additions to norbornene and a number of dienes.



(216)



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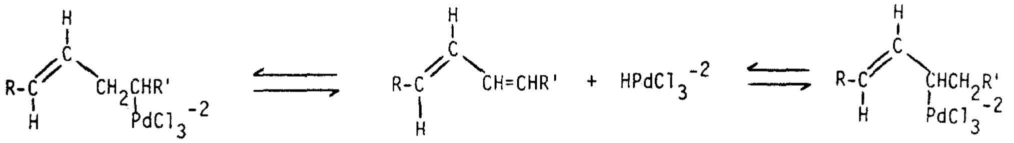
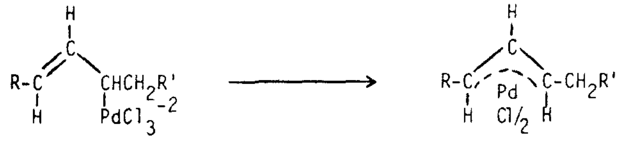


(218)



(219)

The reactions of organopalladium compounds and terminal acetylenes has been reported to afford substitution products, but only in low yield (eqn 220).[345] Relatively little work has been reported on the reactions of acetylenes and organopalladium compounds.

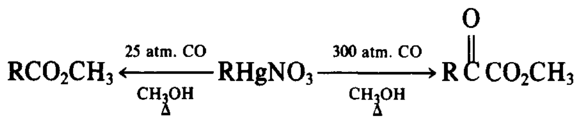
$$RHgOAc + C_6H_5C{\equiv}CH \xrightarrow{Pd(OAc)_2} C_6H_5C{\equiv}CR \qquad (220)$$

To summarize, few organomercurials will directly add to olefins or acetylenes, but a large number of useful reactions have been reported involving the generation of free radicals or organopalladium compounds from organomercurials, and their subsequent addition to olefins or substitution of vinyl hydrogens. Since these reactions tolerate a substantial number of important organic functional groups, they possess considerable potential in organic synthesis.

7. CARBONYLATION

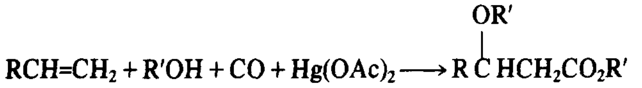
The direct carbonylation of organomercurials is quite difficult, but can prove useful for the synthesis of β-alkoxy carboxylic acid derivatives, carbonates, urethanes and ureas. A number of transition metal reagents catalyze carbonylation processes and afford a variety of carboxylic acids and esters, as well as ketones.

The direct reaction of organomercurials and carbon monoxide generally requires high temperatures and pressures. Depending on the carbon monoxide pressure, one can obtain either simple carboxylic acid derivatives[346,347] or α-keto carboxylic acids[348] in low yields (eqn 221). β-Alkoxy carboxylic esters can be



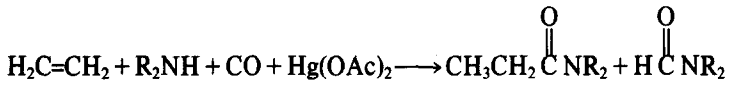
$$RCO_2CH_3 \xleftarrow[CH_3OH,\ \Delta]{25\ atm.\ CO} RHgNO_3 \xrightarrow[CH_3OH,\ \Delta]{300\ atm.\ CO} R\overset{O}{\overset{\|}{C}}CO_2CH_3 \qquad (221)$$

obtained in similar fashion via alkoxymercuration–carbonylation of olefins (eqn 222).[346,349–352] In the



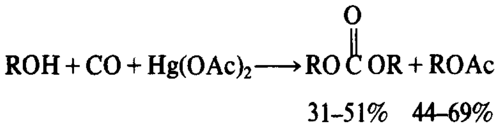
$$RCH{=}CH_2 + R'OH + CO + Hg(OAc)_2 \longrightarrow R\overset{OR'}{\overset{|}{C}}HCH_2CO_2R' \qquad (222)$$

presence of amines, simple amides and formamides are obtained (eqn 223).[353]



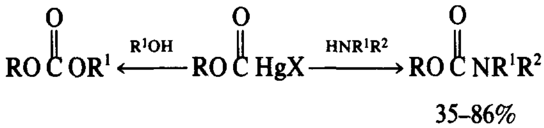
$$H_2C{=}CH_2 + R_2NH + CO + Hg(OAc)_2 \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}NR_2 + H\overset{O}{\overset{\|}{C}}NR_2 \qquad (223)$$

The direct reaction of mercury salts and alcohols or amines affords a useful alternative to the isonitrile procedures discussed earlier in Section 3 for the synthesis of carbonates, urethanes and ureas. Alcohols give modest yields of carbonates at 100 atmospheres of carbon monoxide and temperatures of 200–220° (eqn 224).[354–356] The reaction of carboalkoxymercurials and either alcohols or amines affords



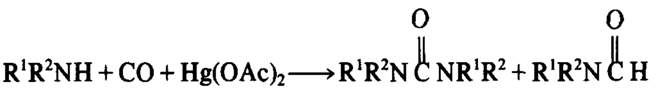
$$ROH + CO + Hg(OAc)_2 \longrightarrow \underset{31\text{–}51\%}{RO\overset{O}{\overset{\|}{C}}OR} + \underset{44\text{–}69\%}{ROAc} \qquad (224)$$

unsymmetrical carbonates[233,357] or urethanes[233] (eqn 225), while the direct carbonylation of amines



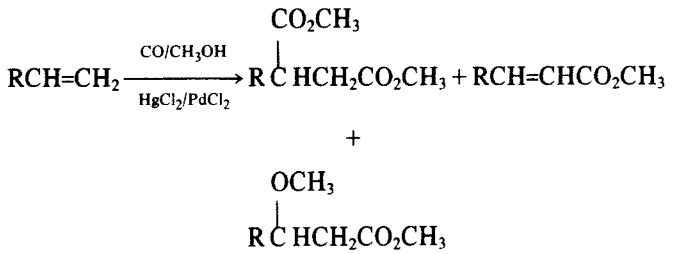
$$RO\overset{O}{\overset{\|}{C}}OR^1 \xleftarrow{R^1OH} RO\overset{O}{\overset{\|}{C}}HgX \xrightarrow{HNR^1R^2} \underset{35\text{–}86\%}{RO\overset{O}{\overset{\|}{C}}NR^1R^2} \qquad (225)$$

provides ureas and/or formamides depending on the amine employed and the reaction conditions (eqn 226).[358–364]



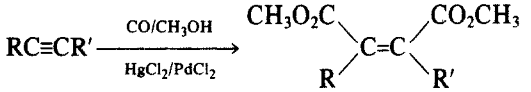
$$R^1R^2NH + CO + Hg(OAc)_2 \longrightarrow R^1R^2N\overset{O}{\overset{\|}{C}}NR^1R^2 + R^1R^2N\overset{O}{\overset{\|}{C}}H \qquad (226)$$

Transition metal reagents have been very effectively employed to extend the synthetic utility of these carbonylation reactions. We have already seen the use of carboalkoxymercurials in the Heck reaction. The direct reaction of olefins, alcohols, mercuric chloride and palladium chloride affords succinate esters instead, accompanied by α,β-unsaturated esters and β-methoxy esters (eqn 227).[345] The same



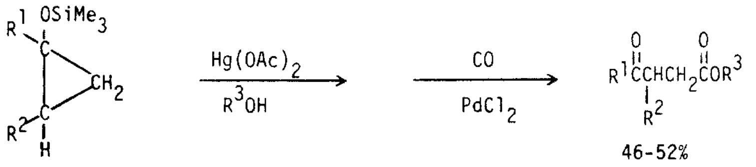
$$\mathrm{RCH{=}CH_2 \xrightarrow[HgCl_2/PdCl_2]{CO/CH_3OH} R\overset{\displaystyle CO_2CH_3}{\overset{|}{C}}HCH_2CO_2CH_3 + RCH{=}CHCO_2CH_3 + R\overset{\displaystyle OCH_3}{\overset{|}{C}}HCH_2CO_2CH_3} \tag{227}$$

reaction with alkynes proceeds with only catalytic amounts of palladium and yields maleates (eqn 228).



(228)

The palladium promoted carbonylation of alkylmercurials proceeds with predominant retention of configuration, but generally gives only low yields of products.[365] Nevertheless, the mercuration and subsequent palladium promoted carbonylation of cyclopropyl trimethylsilyl ethers provides a novel route to γ-keto esters (eqn 229).[366] In the absence of carbon monoxide, α-methylene ketones are obtained by palladium hydride elimination (eqn 230).



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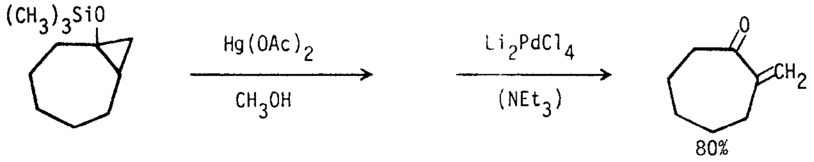
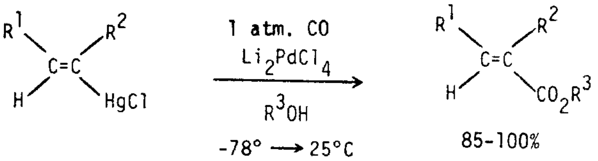


(230)

The carbonylation of vinylmercurials proceeds in much higher yields (eqn 231).[367] Furthermore, the reaction becomes catalytic in palladium when either cupric chloride[367] or ferric chloride[368] are added. By employing 2–5% aqueous THF as the solvent, α,β-unsaturated carboxylic acids can be obtained instead (eqn 232).[367] These carbonylation reactions provide a novel route to the butenolide ring system (eqn 233).[369] Attempts to catalyze the carbonylation of vinylmercurials by $Cl_2Pd(PPh_3)_2$ at elevated temperatures and pressures have generally given only low yields of the corresponding unsaturated esters.[370]



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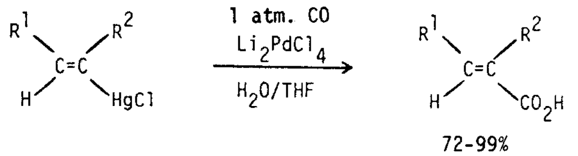
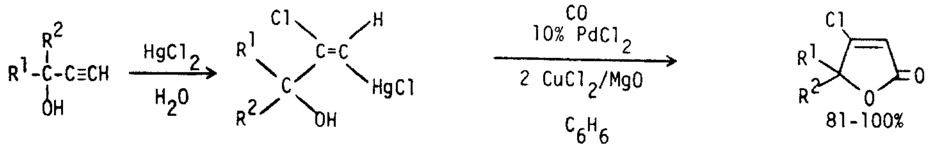
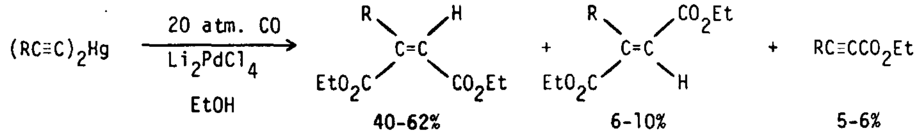


(232)



(233)

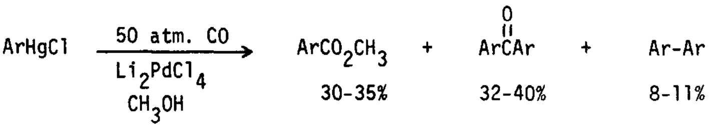
The palladium promoted carbonylation of dialkynylmercurials unexpectedly affords mainly maleate esters containing small amounts of the corresponding fumarate and acetylenic esters (eqn 234).[371]


(234)

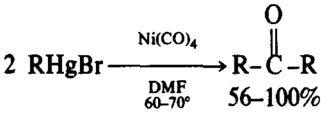
Surprisingly little work has been reported on the carbonylation of arylmercurials. One report indicates that the corresponding carboxylic acids, acid chlorides and esters can be obtained by using palladium chloride and carbon monoxide in appropriate solvents, but low yields were the rule.[372] Considerably better results were obtained by employing catalytic amounts of $Cl_2Pd(PPh_3)_2$ at elevated temperatures and pressures (eqn 235).[370] In the carbonylation of heterocyclic and ferrocenylmercurials,

$$\mathrm{ArHgX} \xrightarrow[\substack{70\text{-}110^{\circ}\mathrm{C} \\ \mathrm{ROH}}]{\substack{60\text{-}128 \text{ psig CO} \\ \text{cat. } Cl_2Pd(PPh_3)_2}} \underset{10\text{-}99\%}{\mathrm{ArCO_2R}} \qquad (235)$$

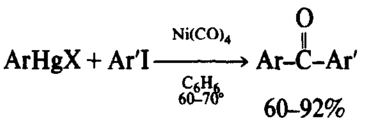
the desired esters are frequently accompanied by comparable amounts of the corresponding symmetrical ketone and some biaryl (eqn 236).[373–375]


$$\mathrm{ArHgCl} \xrightarrow[\substack{Li_2PdCl_4 \\ CH_3OH}]{50 \text{ atm. CO}} \underset{30\text{-}35\%}{\mathrm{ArCO_2CH_3}} + \underset{32\text{-}40\%}{\mathrm{Ar\overset{\overset{O}{\|}}{C}Ar}} + \underset{8\text{-}11\%}{\mathrm{Ar\text{-}Ar}} \qquad (236)$$

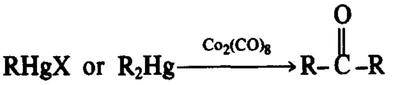
Several other transition metals have been employed effectively in the carbonylation of organomercurials. For example, nickel tetracarbonyl in DMF affords high yields of symmetrical ketones from both primary alkyl- and arylmercuric bromides (eqn 237).[376] Both the halide present in the organomercurial


$$2\ \mathrm{RHgBr} \xrightarrow[\substack{DMF \\ 60\text{-}70^{\circ}}]{Ni(CO)_4} \underset{56\text{-}100\%}{\mathrm{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}R}} \qquad (237)$$

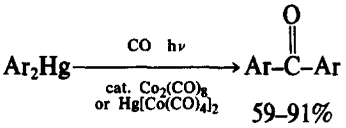
and the solvent are critical to the success of this reaction. By employing arylmercuric halides (chloride or bromide) and aryl iodides in benzene, unsymmetrical diaryl ketones are obtained in high yield (eqn 238).[376,377]


$$\mathrm{ArHgX + Ar'I} \xrightarrow[\substack{C_6H_6 \\ 60\text{-}70^{\circ}}]{Ni(CO)_4} \underset{60\text{-}92\%}{\mathrm{Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ar'}} \qquad (238)$$

In similar fashion, dicobalt octacarbonyl can be utilized for the preparation of both symmetrical dialkyl and diaryl ketones (eqn 239).[378–381] Best results are obtained from arylmercurials. This reaction

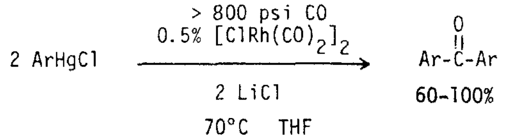

$$\mathrm{RHgX \text{ or } R_2Hg} \xrightarrow{Co_2(CO)_8} \mathrm{R\text{-}\overset{\overset{O}{\|}}{C}\text{-}R} \qquad (239)$$

becomes catalytic in cobalt when carried out by photolysis in the presence of either $Co_2(CO)_8$ or $Hg[Co(CO)_4]_2$ (eqn 240).[381,382]


$$\mathrm{Ar_2Hg} \xrightarrow[\substack{\text{cat. } Co_2(CO)_8 \\ \text{or } Hg[Co(CO)_4]_2}]{CO\ h\nu} \underset{59\text{-}91\%}{\mathrm{Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ar}} \qquad (240)$$

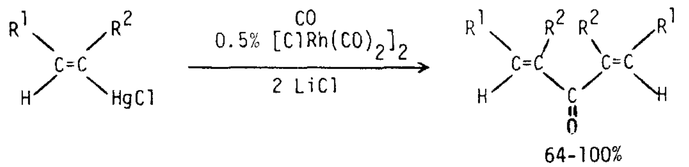
Rhodium catalysts have also shown promise in organomercurial carbonylation reactions. Wilkinson's catalyst smoothly effects the carbonylation of alkyl- and phenylmercuric acetates to the corresponding esters or acids (eqn 241).[370,383] Symmetrical ketones can also be obtained using rhodium catalysts. For example, diaryl ketones are easily obtained from arylmercuric chlorides using $RhCl_3 \cdot 3H_2O$,[384] $ClRh(CO)(PR_3)_2$[384] or $[ClRh(CO)_2]_2$[385] as catalysts, although the latter catalyst appears to be the most efficient (eqn 242). This same catalyst converts vinylmercuric chlorides to divinyl ketones in excellent yield at room temperature and atmospheric pressure (eqn 243).[385]

$$RHgOAc \xrightarrow[CH_3OH]{\substack{CO \\ cat.\ ClRh(PPh_3)_3}} RCO_2CH_3 + RCO_2H \qquad (241)$$



$$2\ ArHgCl \xrightarrow[\substack{2\ LiCl \\ 70°C \quad THF}]{\substack{> 800\ psi\ CO \\ 0.5\%\ [ClRh(CO)_2]_2}} \underset{60\text{-}100\%}{Ar\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ar} \qquad (242)$$

converts vinylmercuric chlorides to divinyl ketones in excellent yield at room temperature and atmospheric pressure (eqn 243).[385]



(243)

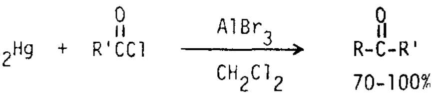
In summary, while the direct carbonylation of organomercurials is difficult and tends to give low yields, the reaction of mercury salts and alcohols or amines provides a useful route to carbonates, urethanes and ureas. By employing transition metal reagents of palladium, nickel, cobalt or rhodium, the scope of these carbonylation reactions is greatly expanded and a variety of useful carbonyl-containing products can be obtained in high yield, including carboxylic acids and esters, as well as ketones. The following section discusses alternate approaches to ketones via acylation reactions.

8. ACYLATION

The acylation of organomercurials provides a useful approach to ketones, as well as enol esters. It can be effected directly with acyl halides or by adding a palladium(O) catalyst or aluminum halides.

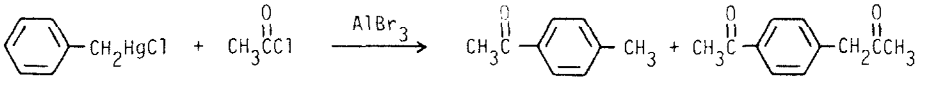
The direct acylation of the carbon–mercury bond is sufficiently difficult that a number of other functional groups that one might find present in organomercurials will react preferentially. Thus, mercurated alcohols, phenols and amines acylate more readily on the heteroatom.

Simple alkylmercurials react with acid halides only under forcing conditions to give ketones, but the addition of aluminum bromide gives high yields at room temperature (eqn 244).[386] This reaction can also be catalyzed by adding $Pd(PPh_3)_4$ in HMPA.[387]

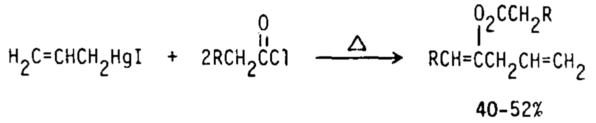


$$R_2Hg + R'\overset{O}{\overset{\|}{C}}Cl \xrightarrow[CH_2Cl_2]{AlBr_3} \underset{70\text{-}100\%}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}R'} \qquad (244)$$

The acylation of benzylmercuric chloride[388] and allylmercuric iodide[389] gave unexpected results (eqns 245, 246). The two aryl ketones obtained in the former reaction appear to arise via initial acylation on the aromatic ring so as to form 6-acetyl-3-methylene-1,4-cyclohexadiene which either isomerizes or undergoes a second acylation. The enol ester product of the latter reaction is apparently formed by generation



(245)

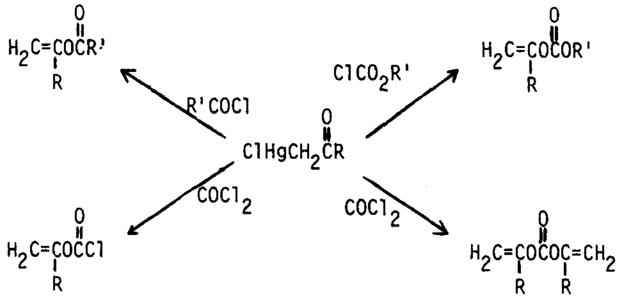


$$H_2C{=}CHCH_2HgI + 2RCH_2\overset{\overset{O}{\|}}{C}Cl \xrightarrow{\Delta} RCH{=}\overset{O_2CCH_2R}{\overset{|}{C}}CH_2CH{=}CH_2 \quad 40\text{-}52\%$$

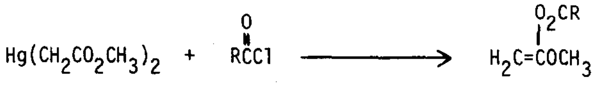
(246)

of a ketene from the acid chloride, followed by insertion of the ketene into the allyl-mercury bond to generate an α-mercurated ketone which undergoes further acylation on oxygen.

In fact, the acylation of α-mercurated carbonyl compounds provides a very useful route to a wide variety of enol esters (eqns 247, 248).[62,64,95,289,390–394]



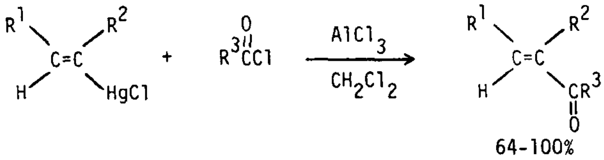
(247)



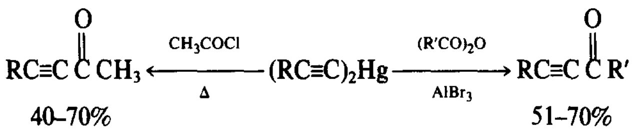
$$Hg(CH_2CO_2CH_3)_2 + R\overset{\overset{O}{\|}}{C}Cl \longrightarrow H_2C{=}\overset{O_2CR}{\overset{|}{C}}OCH_3$$

(248)

Unsaturated organomercurials also undergo acylation quite readily. For example, vinylmercurials can be acylated by acid chlorides in excellent yield by adding aluminum chloride (eqn 249).[395] Dialkynylmercurials undergo acylation by acid chlorides upon simply refluxing in heptane, or one can employ acid anhydrides plus aluminum bromide (eqn 250).[396]



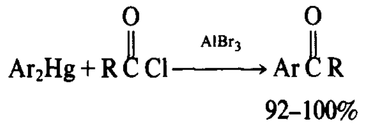
(249)



$$\underset{40\text{–}70\%}{RC{\equiv}C\overset{\overset{O}{\|}}{C}CH_3} \xleftarrow[\Delta]{CH_3COCl} (RC{\equiv}C)_2Hg \xrightarrow[AlBr_3]{(R'CO)_2O} \underset{51\text{–}70\%}{RC{\equiv}C\overset{\overset{O}{\|}}{C}R'}$$

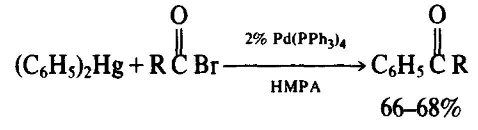
(250)

Although certain heterocyclic mercurials, such as furans, thiophenes and their benzo analogs, react directly with acid chlorides to afford ketones, the majority of arylmercurials react only in the presence of aluminum bromide[386,397,398] or under $Pd(PPh_3)_4$ catalysis[387] (eqns 251, 252).



$$Ar_2Hg + R\overset{\overset{O}{\|}}{C}Cl \xrightarrow{AlBr_3} \underset{92\text{–}100\%}{Ar\overset{\overset{O}{\|}}{C}R}$$

(251)



$$(C_6H_5)_2Hg + R\overset{\overset{O}{\|}}{C}Br \xrightarrow[HMPA]{2\%\ Pd(PPh_3)_4} \underset{66\text{–}68\%}{C_6H_5\overset{\overset{O}{\|}}{C}R}$$

(252)

In general then, a wide variety of ketones can be prepared by the acylation of organomercurials. The acylation of α-mercurated carbonyl compounds proceeds by reaction at oxygen and provides a useful route to a wide variety of enol esters.

CONCLUSION

Organomercurials have been known since the 1850's. Hundreds or perhaps thousands of these compounds are now known, and many are commercially available. A wide variety of synthetic procedures exist for their preparation. These unique organometallics possess a number of characteristics making them attractive as intermediates in organic synthesis. They are generally stable to air, protic solvents, dilute acids and bases, and elevated temperatures, and accommodate essentially all important organic functional groups. Their toxicity is not generally a problem since they are usually high melting, crystalline, relatively non-volatile solids.

Until recently there were relatively few transformations of organomercurials which were of interest to the synthetic organic chemist. In the past dozen years however, with the rapid development of transition metal organometallic chemistry, a number of useful new synthetic transformations have been reported. These reactions generally take advantage of the ease with which organomercurials undergo transmetallation by a variety of transition metal reagents, particularly palladium salts, to generate the corresponding transition metal organometallic. These new organometallics can also accommodate a wide range of organic functionalities, but are much more reactive and afford a number of useful and often unique synthetic transformations. Many of these reactions can also be effected using only catalytic amounts of the transition metal reagent. At present a large number of reactions of organomercurials useful in organic synthesis are known. This report has attempted to briefly summarize some of the more important of these reactions. For a more complete discussion of the role of organomercurials in organic synthesis, the reader is referred to the forthcoming book by the present author on this topic. A complete review of the use of organomercurials as divalent carbon transfer reagents and in solvomercuration-demercuration reactions can also be found therein. From this review it is hoped that the reader has gained a deeper appreciation of the many ways in which organomercurials can be utilized in organic synthesis and will be encouraged to employ these reactions in the solution of synthetic organic problems.

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