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Advances in the methods of synthesis of organic compounds of mercury

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Abstract. New data on the methods of synthesis and practical applications of organic compounds of mercury are surveyed and treated systematically. The bibliography includes 180 references.

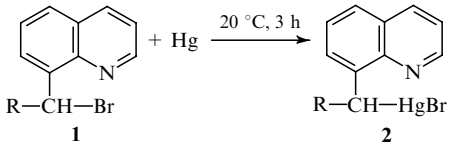
I. Introduction

The chemistry of organic compounds of mercury is one of the most extensive and thoroughly investigated fields of organometallic chemistry.[1–7] Organomercury compounds (OMC) proved to be convenient objects for the solution of a series of fundamental problems of theoretical organic chemistry.[8,9] They are also of practical importance, particularly in organic synthesis.[3,7,10–12]

The original studies, published up to 1980, have been dealt with systematically in reviews[4,5,9] and monographs,[1–3,6–8] but during the last 15 years many new studies on the synthesis of OMC have been published. Certain data on particular aspects of the chemistry of OMC during the period indicated have been surveyed in reviews[10–12] and dissertations.[13–17] In the present review, a systematic and critical account is given of new and most significant, from our point of view, literature data on the methods of synthesis and applications of OMC.

II. Insertion of a mercury atom in a C – Hal bond

The method of synthesis of OMC by the insertion of a Hg atom in a C – Hal bond was historically the first employed,[1] but it has still not lost its importance because of the availability of the initial reactants and the relative simplicity of the preparative use of the reaction. Thus the interaction of 8-(1-bromoalkyl)quinolines **1** with metallic mercury afforded[18] the corresponding bromomercurioquinoline derivatives **2**, which are convenient models for the study of mechanisms of the S_E1-*N* type.[8,18]



1 **2**

R = H, Me.

The reactions of hexahalotoluenes with metallic mercury have been investigated.[19,20] Thus the interaction of pentabromobenzyl bromide (**3**) with mercury in benzene results in the formation of pentabromobenzylmercury bromide (**4**).

$$\underset{\mathbf{3}}{C_6Br_5CH_2Br} + Hg \xrightarrow{20\ ^\circ C} \underset{\mathbf{4}}{C_6Br_5CH_2HgBr}.$$

On the other hand, pentachlorobenzyl chloride **5** does not react with mercury under these conditions [when the reaction mixture is irradiated with UV light, 1,2-bis(pentachlorophenyl)ethane is formed].

In the presence of a catalyst ($Et_4N^+Br^-$, $Et_4N^+I^-$, or NaBr), the bromide **3** and the chloride **5** react with mercury to form symmetrical OMC — bis(pentabromobenzyl)- and bis(pentachlorobenzyl)mercury. On UV irradiation, the latter decompose with liberation of mercury and the formation of 1,2-bis(pentahalophenyl)ethanes (on irradiation with UV light for 2 h, compound **4** does not change). The influence of reaction conditions (solubility, the presence of a catalyst and atmospheric oxygen, illumination) on the composition and yield of the products of the interaction of the halogenated benzyl halides **3** and **5** with metallic mercury has been studied.[20] The optimum method of synthesis of type **4** benzylmercury derivatives has been proposed (DMF, Br^-, darkness, absence of atmospheric oxygen, 20 °C).

The interaction of metallic mercury with propargyl halides **6** has been investigated.[21] On ethyne – allene rearrangement in a sealed tube under a nitrogen atmosphere and in sunlight in the course of 2 h,[8] the allenyl derivatives of mercury **7** are formed. Their structure has been confirmed by IR and NMR spectroscopic data.

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$$R^1C{\equiv}C{-}CR^2R^3X + Hg \xrightarrow{h\nu} R^2R^3C{=}C{=}CR^1HgX$$

6 **7**

$R^1 = R^2 = R^3 = H$, X = I; $R^1 = R^3 = H$, R^2 = Me, X = I;
R^1 = Ph, R^2 = Me, R^3 = H, X = I; $R^1 = H$, $R^2 = R^3$ = Me, X = Br.

Other derivatives **6** form under these conditions a mixture of the corresponding propargylmercury derivatives **8** and the allenyl derivatives **7**.[21]

$$\mathbf{6} + Hg \xrightarrow{h\nu} R^1C{\equiv}C{-}CR^2R^3HgX + \mathbf{7}$$

8

R^1 = Ph, $R^2 = R^3 = H$, X = Br; R^1 = Me, $R^2 = R^3 = H$, X = I;
R^1 = Ph, $R^2 = R^3 = H$, X = I; $R^1 = (CH_2)_3OAc$, $R^2 = R^3 = H$, X = I.

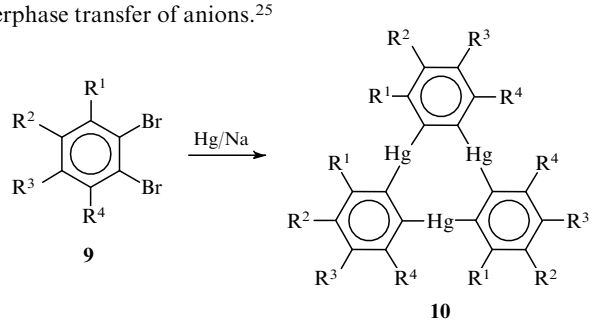
The synthesis of allyl ketones, which proceeds *via* the formation of allylic OMC, has been described.[22,23]

$$CH_2{=}CH{-}CH_2I + Hg \xrightarrow{THF} CH_2{=}CH{-}CH_2HgI \xrightarrow[-HgICl]{RCOCl} CH_2{=}CH{-}CH_2{-}C(O)R$$

(50% – 82%)

R = Me, Ph, 4-ClC_6H_4, 2-FC_6H_4.

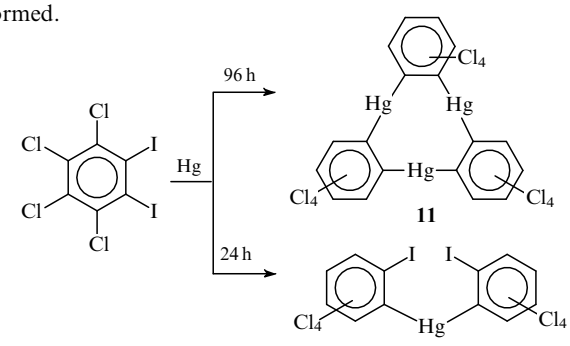
The substitution of a halogen by mercury is known [3] to occur only on interaction of aryl halides with an alkali metal amalgam; the reaction with metallic mercury does not take place. The reactions of sodium amalgam with a series of aryl halides have been studied.[24] Thus the reaction of *o*-dibromobenzenes **9** with Hg/Na in THF for 2 h at 80 °C leads to *o*-arylenemercury trimers **10**, which are of preparative interest as crown-compounds for the interphase transfer of anions.[25]



9 **10**

$R^1 = R^2 = R^3 = R^4 = H$; $R^1 = R^3 = R^4 = H$, R^2 = Me;
R^1 = Me, $R^2 = R^3 = R^4 = H$; $R^1 = R^4 = H$, $R^2 = R^3$ = Me;
$R^1 = R^2 = H$, $R^3 = R^4$ = OMe; $R^1 = R^2 = R^3 = R^4$ = Me.

Compound **11** is formed as a result of the reaction of tetrachloro-1,2-diiodobenzene with mercury on heating (100 °C) in a sealed tube for four days.[24] When the reaction time is reduced to 24 h, only bis(3,4,5,6-tetrachloro-2-iodophenyl)mercury is formed.



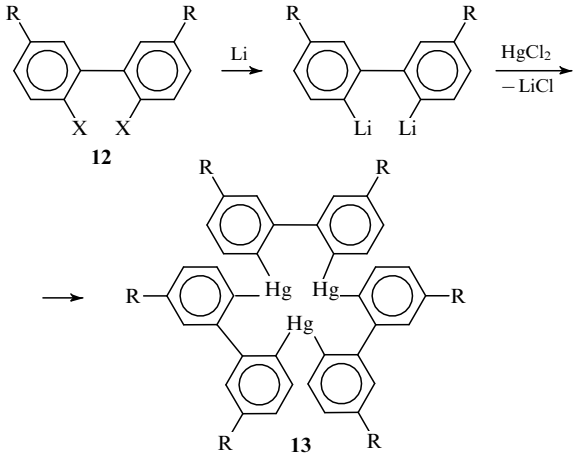
11

In conclusion of this section, one should note that, despite the long history of the use of reactions of the above types in syntheses of OMC, the mechanisms of these reactions have been scarcely studied.[3–8] However, on the basis of the conditions (temperature, irradiation) under which mercury interacts with halogen-containing compounds, it is possible to make a choice in favour of a radical mechanism of the above reactions. Here the greatest activity is shown by iodides, while the bromo-derivatives react only when the carbon – bromine bond has been activated, for example by conjugation with a multiple bond,[18–21] and chlorides are altogether inactive. Apparently, the limits of the applicability of the method of synthesis of OMC under consideration are determined primarily by the availability of the corresponding halo-derivatives and are not restricted by the choice of reaction conditions, which are standard in most cases.[3]

III. Substitution by mercury of other metal atoms and functional groups

This approach to the synthesis of OMC is universal because it makes it possible, by varying the structures of the initial reactants, to synthesise in one stage a wide variety of mercury-containing substances with the required combinations of substituents at the mercury atom.

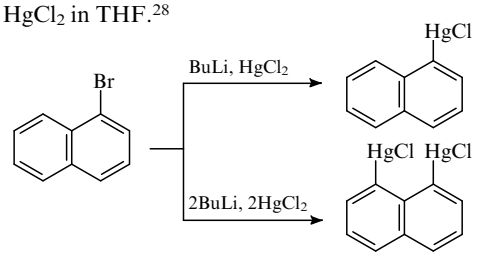
Thus bis(1-bicyclo[1.1.0]butyl)mercury has been obtained [26] in 75% yield by the reaction of the 1-lithiobicyclo-[1.1.0]butane – tetramethylethylenediamine (TMEDA) complex with mercury(II) chloride in THF. The reaction of substituted 2,2′-dihalobiphenyls **12** with lithium or butyllithium [24] and also of biphenylene with the BuLi – TMEDA complex led to the synthesis [27] of the corresponding organolithium compounds, which on subsequent treatment with $HgCl_2$ in ether give rise to cyclic biphenylenemercury trimers **13** in low (2% – 3%) yields.



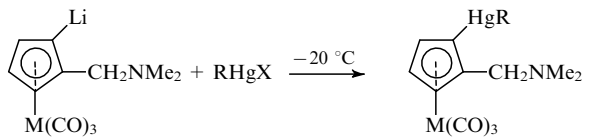
12 **13**

R = H, Me, Et; X = Cl, Br.

1-Naphthylmercury chloride and 1,8-di(chloromer-curio)-naphthalene (depending on the molar reactant ratio) have been synthesised similarly by the reaction of 1-bromonaphthalene with butyllithium in a hexane – ether mixture with subsequent addition of $HgCl_2$ in THF.[28]



The optimum conditions have been found [29] for the reactions of lithium derivatives of (dimethylaminomethylcycloheptadienyl)tricarbonyl-manganese and -rhenium **14** with organic and metal carbonyl mercury salts, leading to the formation of symmetrical [R = $(CO)_3MC_5H_3(CH_2NMe_2)$] and asymmetric (R = Cl, Br) OMC **15**.

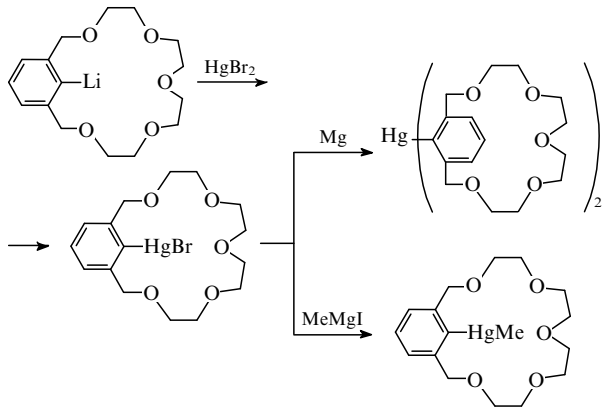


14 **15** (60% – 80%)

M = Mn, Re; R = Cl, Br, $(CO)_3MC_5H_3(CH_2NMe_2)$; X = Cl, Br.

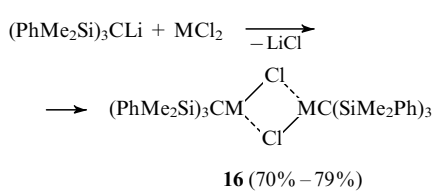
The lithium salts **14** have been synthesised *in situ* by the reaction of BuLi with the corresponding (dimethylaminomethylcyclopentadienyl)tricarbonylmetal derivatives in THF at −70 °C. Compounds **15** were characterised by ^1H and ^{13}C NMR as well as IR spectroscopic data. Under these conditions, a downfield shift of the signals due to the CH_2 and Me groups in the ^1H NMR spectra relative to the signals of these groups in the initial complexes was observed. According to Suleimanov *et al.*,[29] the reason for this is the coordination of the nitrogen atom to the mercury atom, which has been confirmed by X-ray diffraction (XRD) study of the symmetrical OMC **15**. It was established that the length of the Hg – C bond (2.042 Å) is reduced compared with the statistical mean value 2.07 Å. The dimethylaminomethyl fragment has the conformation in which the lone pairs of the nitrogen atoms in the molecules of compound **15** are directed towards the mercury atom, but the Hg – N distance (2.933 Å) corresponds to only a weak secondary bond.

[2-(Bromomercurio)-1,3-xylidene]-18-crown-5 has been synthesised by the reaction of (2-lithio-1,3-xylidene)-18-crown-5 with $HgBr_2$ in THF and its reactions on treatment with magnesium and methylmagnesium iodide have been studied.[30]



The existence of an intramolecular coordinate bond Hg···O with two out of the five oxygen atoms has been established by X-ray diffraction for all the OMC presented.[30] Similar reactions have been achieved with (2-lithio-1,3-xylidene)15-crown-4.[30]

The organosilicon compounds **16** have been obtained by the reaction of tris(dimethylphenylsilyl)methyllithium with the chloride of the corresponding metal in an ether – THF mixture.[31]



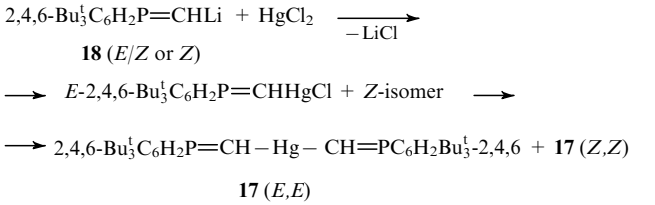
16 (70% – 79%)

M = Zn, Cd, Hg.

The structures of the organometallic compounds obtained have been established by X-ray diffraction. They proved to be dimeric[31] as a result of the formation of chloride bridges.

The phosphoalkenylmercurated compounds **17** in the form of the *E*- and *Z*-isomers have been synthesised in 30% – 63% yields from the corresponding lithium salts **18** and mercury chloride in a hexane – THF mixture (Scheme 1).[32]

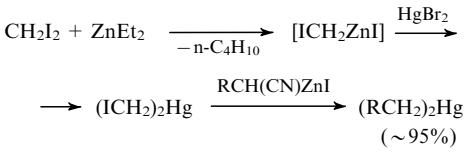
Scheme 1



It was established that the *Z*-isomers are thermodynamically more stable than the *E*-isomers, which are converted into the *Z*-isomers after a time.

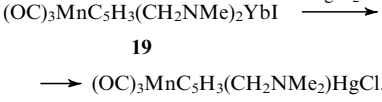
A laboratory method has been developed recently[33] for the synthesis of Bu^t_2Hg by the reaction of Bu^tMgCl with $HgCl_2$ in THF. The yield of bis(*tert*-butyl)mercury was then 73%.

A method has been proposed for the synthesis[34] of functionally substituted OMC involving the use of organozinc compounds[18] *via* the intermediate formation of bis(iodomethylene)mercury.



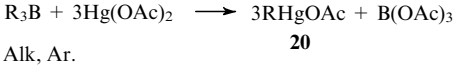
R = Bu^n, cyclo-C_5H_{11}, $PhCH_2$, $AcO(CH_2)_3$, $EtOCO(CH_2)_3$, $NC(CH_2)_3$, $Cl(CH_2)_4$, $Br(CH_2)_3P(O)(EtO)_2CH_2CH_2$.

1-Chloromercurio-2-(dimethylaminomethyl)cymantrene has been obtained in 73% yield the reaction of [2-(dimethylaminomethyl)cymantrenyl]ytterbium iodide (**19**) or bis[2-(dimethylaminomethyl)cymantrenyl]ytterbium with $HgCl_2$ in THE.[35]



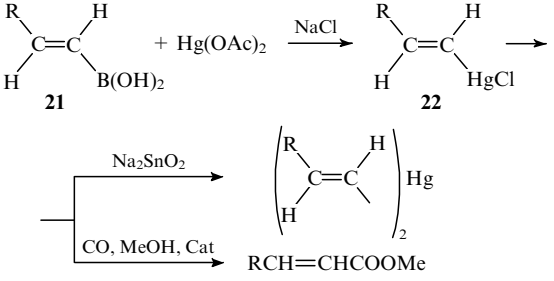
When mercury acetate is refluxed with tricarbonylcyclopentadienylmanganese in alcohol (molar reactant ratio 5 : 1), tricarbonyl[η^5-pentakis(acetoxymercurio)cyclopentadienyl]manganese is formed.[36] It was subsequently used in the syntheses of a series of pentasubstituted derivatives of cymantrene.[36]

Organylmercury acetates **20** are formed readily as a result of the transmetallation of organoboron compounds with mercury acetate.[37]



R = Alk, Ar.

The interaction of the *E*-isomer **21** with mercury acetate in THF at room temperature and subsequent treatment with sodium chloride lead to the organomercurioalkenes **22** with retention of the configuration.[38] On treatment with an alkaline solution of Na_2SnO_2 in a THF – water mixture, the latter are readily symmetrised with formation of fully substituted mercurioalkenes having the *E*-configuration.[38]



R = C_8H_{17}, $Cl(CH_2)_3$, $I(CH_2)_3$, $AcO(CH_2)_8$, $PhO(CH_2)_3$.

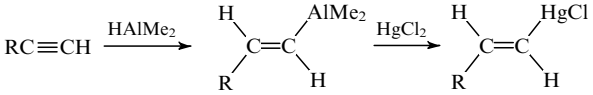
The reaction of compound **22** with CO and MeOH in the presence of a catalyst (Li_2PdCl_4 and MgO or Pr^i_2NEt) afforded a mixture of the *cis*- and *trans*-isomers of the corresponding unsaturated acid esters in 70% – 80% yields.[39]

Treatment of tris(dimethoxyboryl)methane with mercury salts in THF results in the substitution of the dimethoxyboryl groups by HgX with formation of trimercurated methane.[40]

$$HC[B(OMe)_2]_3 + 3HgX_2 \longrightarrow HC(HgX)_3$$

X = F, Cl, Br, OAc.

The interaction[41] of terminal alkynes with organoaluminium hydrides in the presence of Cp_2ZrCl_2 proceeds regio- and stereoselectively with formation of (*E*)-alkenylalanes, which react with $HgCl_2$ in THF to form the corresponding (*E*)-alkenylmercury chlorides.



R = C_8H_{17}, Ph, CH_2=CMe, C_6H_{13}.

The exchange of tin for mercury as a result of the reaction

$$RSCH_2SnBu_3 + HgCl_2 \xrightarrow{Me_2CO} RSCH_2HgCl + ClSnBu_3$$

R = Me, Ph

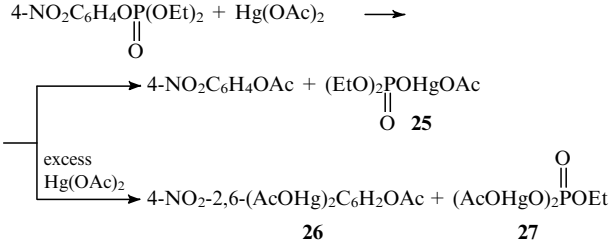
has been achieved.[42] The yield of the reaction products is 90%.

It has been shown that[43] the demetallation reactions of the tributylstannyl derivatives of α,β-unsaturated carboxylic acids **23** on treatment with mercury salts proceed selectively with formation (after treatment of the reaction mixture with potassium chloride) of butylmercury chloride and the corresponding acids **24**. The mercuration of the double bonds was not observed in a single instance.

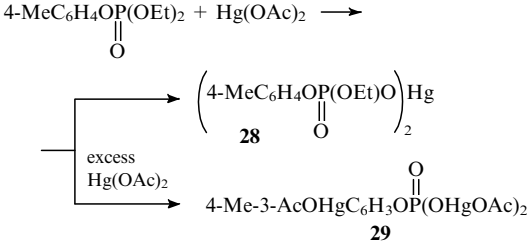
$$\underset{\mathbf{23}}{RCH{=}CHCOOSnBu_3} + HgX_2 \xrightarrow{KCl} BuHgCl + \underset{\mathbf{24}}{RCH{=}CHCOOH}$$

R = H, Me, Ph; X = Cl, OAc.

The interaction[44] of organophosphorus compounds with mercury acetate has been studied. The structure of the products formed depends on the reactant ratio and the reaction conditions. Thus the reaction of equimolar amounts of diethyl *p*-nitrophenyl phosphate and $Hg(OAc)_2$ in hexane or toluene leads to *p*-nitrophenyl acetate and the mercury salt of the phosphate **25**.

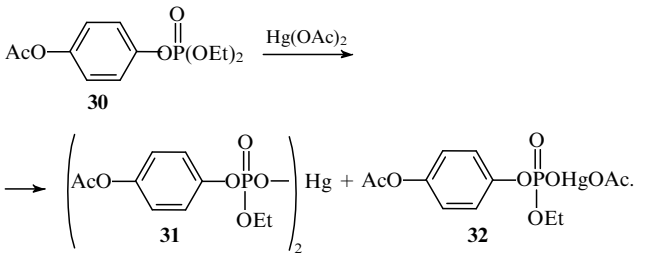


When the reaction is carried out in the presence of an excess of mercury acetate in acetic acid and on heating, compounds **26** and **27** are formed. The interaction of equimolar amounts of diethyl *p*-tolyl phosphate and mercury acetate leads to the salt **28**.[44]

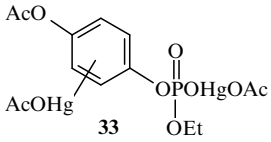


However, when an excess of the mercury salt is employed and the reaction is carried out in acetic acid, the product is compound **29**. The reaction of mercury acetate proceeds similarly also with other phosphates.[44]

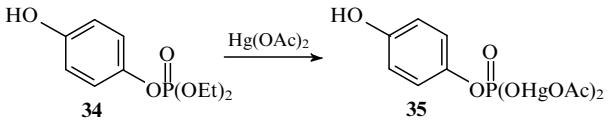
The interaction of equimolar amounts of compound **30** and mercury acetate at 20 °C affords a mixture of the products **31** and **32**.



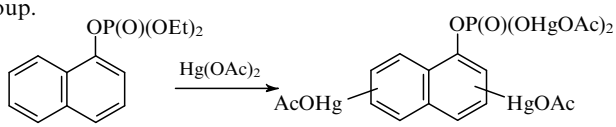
In the presence of an excess of mercury acetate, the product of mercuration in the aromatic ring, namely compound **33**, is formed together with compounds **31** and **32**.



In the reaction of the phosphate **34** with mercury acetate, the only product is compound **35** regardless of the molar reactant ratio.



The interaction of α-naphthyl phosphate with mercury acetate leads to the mercuration of the aromatic ring and simultaneously to the substitution of the ethyl group by the mercurioacetate group.



The synthesis of alkyl- and aryl-mercury chlorides by treating diethoxyphosphinylmercury chloride with acyl peroxides has been described.[45] The reaction is carried out in benzene with heating.

$$(RCOO)_2 + ClHgP(O)(OEt)_2 \longrightarrow \underset{(60\%-88\%)}{RHgCl} + RCOOP(O)(OEt)_2 + CO_2$$

R = $C_{11}H_{23}$, $C_{15}H_{31}$, $C_{17}H_{35}$, Ph, 4-$CH_3C_6H_4$, 4-FC_6H_4, 4-ClC_6H_4.

According to the authors,[45] the reaction proceeds *via* a radical mechanism.

$$(RCOO)_2 \longrightarrow 2RCOO^{\bullet} \longrightarrow 2R^{\bullet} + 2CO_2,$$

$$R^{\bullet} + ClHgP(O)(OEt)_2 \longrightarrow RHgCl + {}^{\bullet}P(O)(OEt)_2,$$

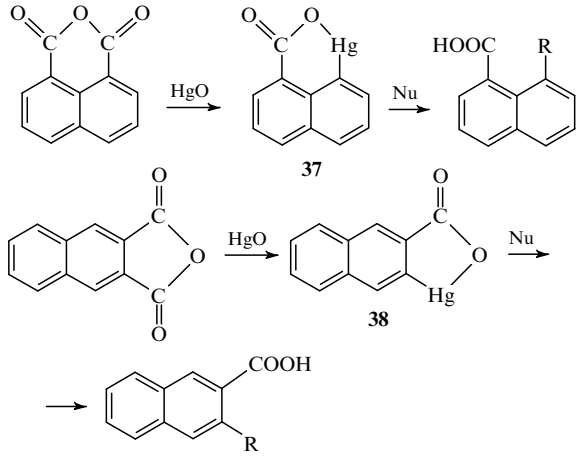
$${}^{\bullet}P(O)(OEt)_2 + (RCOO)_2 \longrightarrow RCOOP(O)(OEt)_2 + RCOO^{\bullet},$$

$${}^{\bullet}P(O)(OEt)_2 + RCOO^{\bullet} \longrightarrow RCOOP(O)(OEt)_2.$$

The mechanism is confirmed by the fact that, in the reaction of *p*-toluyl peroxide with diethoxyphosphinylmercury chloride, a small amount of the mixed anhydride of *p*-toluic acid and diethyl phosphate, *p*-$MeC_6H_4COOP(O)(OEt)_2$ is formed.[45] The anhydride readily polymerises on distillation.

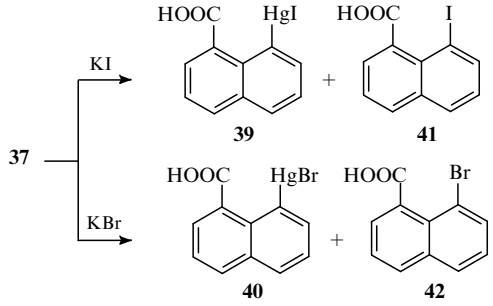
A convenient method has been developed [46] for the synthesis of bis(2,2,6,6-tetramethylpiperidin-4-yl)mercury (**36**) by the electrochemical reduction of 2,2,6,6-tetramethyl-4-oxopiperidine at a mercury cathode in a highly acid medium. Compound **36** is the starting reactant in the synthesis of the stable nitroxyl radical and bis(2,2,6,6-tetramethylpiperidin-4-yl-1-oxyl)mercury,[46] which is used as the mercury label in biochemical research involving the establishment of the structure of proteins.

Mercuration of the anhydrides of naphthalene-1,8- and naphthalene-2,3-dicarboxylic acids with HgO afforded respectively naphtho[1,8-*d*,*e*]-2,1-oxamercuracyclohexan-3-one (**37**) and naphtho[2,3-*d*]-2,1-oxamercuracyclopentan-3-one (**38**) respectively.[47] On interaction with nucleophiles (Nu), they give rise to the corresponding naphthalenecarboxylic acids — convenient synthons for the synthesis of various heterocyclic compounds.

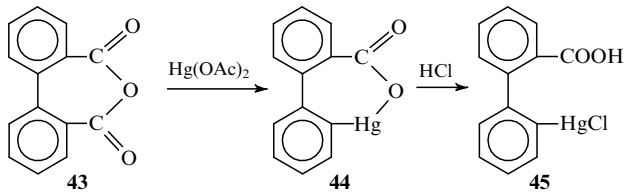


Nu = KI, H_2S, HCN; R = I, SH, CHO.

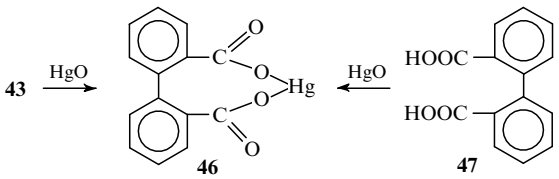
However, a reinvestigation [48] of the nucleophilic demercuration of compound **37** in aqueous acetic acid established that its interaction with potassium iodide or bromide leads to 8-iodo(-bromo)mercurionaphthoic acids **39** and **40** in 30% and 19% yields respectively) and to only traces of demercuration products — 8-iodo- and 8-bromo-naphthoic acids **41** and **42**.



The mercuration product **44** is formed in the reaction of the anhydride of biphenyl-2,2′-dicarboxylic acid (**43**) with mercury acetate in the presence of NaOH. Its treatment with hydrogen chloride affords 2′-chloromercuriobiphenyl-2-carboxylic acid (**45**).[49]



When compound **44** is treated with nucleophiles (KI, H_2S, HCN) in acetic acid, 2′-iodomercurio-, 2′-mercapto-, and 2′-formyl-biphenyl-2-carboxylic acids are formed.[49] The reaction of the anhydride **43** with HgO in an aqueous solution of acetic acid is also described in the same communication. It is shown that the reaction product is the mercury salt of biphenyl-2,2′-dicarboxylic acid **46** (65% yield). This salt has also been obtained by the reaction of the dicarboxylic acid **47** with mercury oxide.[48]



Interesting results have been obtained [50] on refluxing mercury salts HgX_2 with acetic anhydride in acetonitrile. The mercury derivatives of ketene **48** were then synthesised in 60% – 80% yields.

$$Ac_2O + HgX_2 \longrightarrow AcOHg-\underset{\displaystyle XHg}{\overset{|}{C}}=C=O \quad \mathbf{48}$$

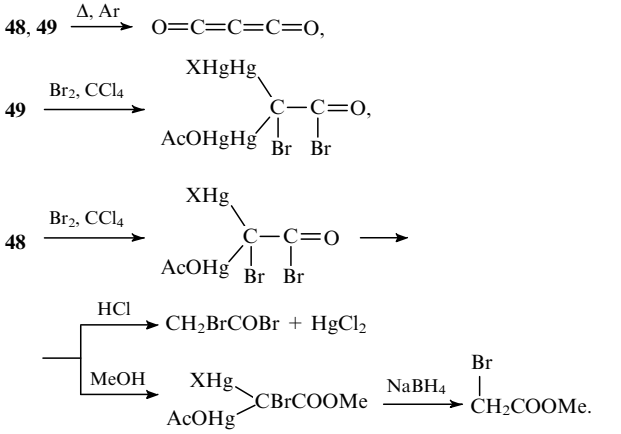
X = AcO, NO_3, ClO_4.

The reaction is accelerated in the presence of traces of sulfuric or perchloric acid. Compounds **48** are also formed when mercury salts HgX_2 are treated with ketene in acetonitrile at 20 °C.

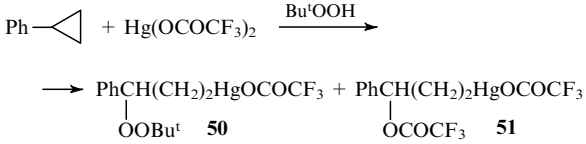
Stable organic derivatives of monovalent mercury **49** have been synthesised in 60% – 80% yields by the reaction of monovalent mercury salts Hg_2X_2 with acetic anhydride under the same conditions.[50]

$$Ac_2O + Hg_2X_2 \longrightarrow AcOHgHg-\underset{\displaystyle XHgHg}{\overset{|}{C}}=C=O \quad \mathbf{49}$$

On treatment with a dilute HCl solution, compounds **49** liberate Hg_2Cl_2 quantitatively, while the ketene derivative **48** dissolves in hydrochloric acid with formation of Hg^{2+} salts. When the mercurated ketenes **48** and **49** are treated with gaseous HCl in the absence of moisture, ketene and acetyl chloride are obtained.[50] The extensive synthetic possibilities of compounds **48** and **49** are demonstrated by the following reactions:[50]



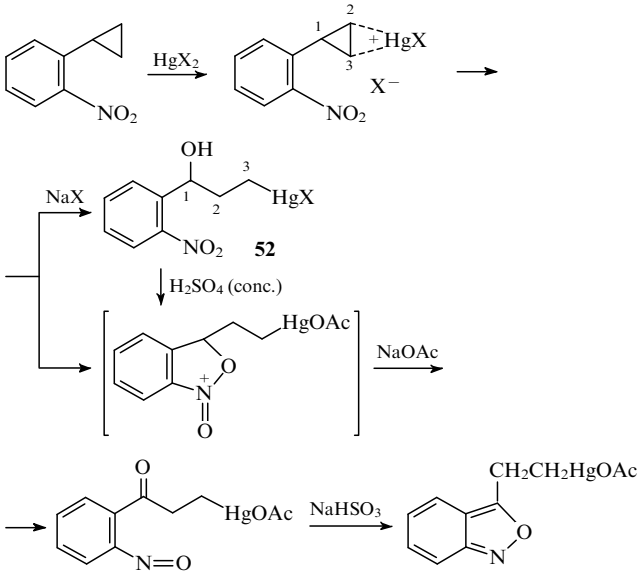
The reactions of various cyclopropane derivatives with mercury salts continue to attract the attention of investigators.[51–57] Thus it has been shown that the interaction of phenylcyclopropane with a mixture of Bu^tOOH and mercury trifluoroacetate in methylene chloride at 20 °C leads to a mixture of the products **50** and **51** in an overall yield of 83%.[51]



When mercury acetate is used, the reaction does not occur.

The interaction of cyclopropane with a mixture of mercury acetate and Bu^tOOH in the presence of $HClO_4$ (CH_2Cl_2, −40 °C, followed by 2 h at 20 °C) and subsequent treatment with KBr lead to a mixture of $Bu^tOO(CH_2)_3HgBr$, $[BrHg(CH_2)_3]_2O$, and AcO.$(CH_2)_3HgBr$, the structures of which have been established on the basis of ^1H, ^{13}C, and ^{199}Hg NMR and IR spectroscopic data.[52]

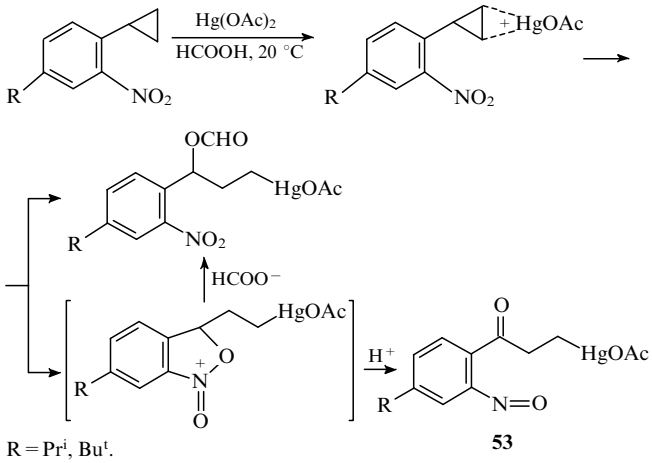
Successive interactions of *o*-nitrocyclopropylbenzene with mercury salts HgX_2 and further with saturated aqueous solutions of NaX led to the synthesis [53, 54] of the corresponding compounds **52**, which are of preparative interest [54, 55] for the synthesis of mercury-containing heterocyclic compounds.



X = NO_2, Cl, AcO.

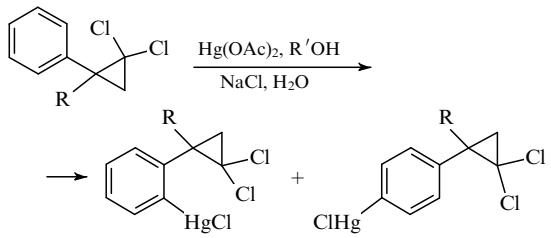
The mode of the conjugate mercuration of substituted *o*-nitrocyclopropylbenzenes by mercury acetate in formic acid depends on the nature of the substituents in the aromatic ring.[56] Under all the conditions investigated, the conjugate mercuration process is accompanied by the conversion of *o*-nitrocyclopropylbenzenes into mercurated *o*-nitrosopropiophenones **53** (Scheme 2).

Scheme 2



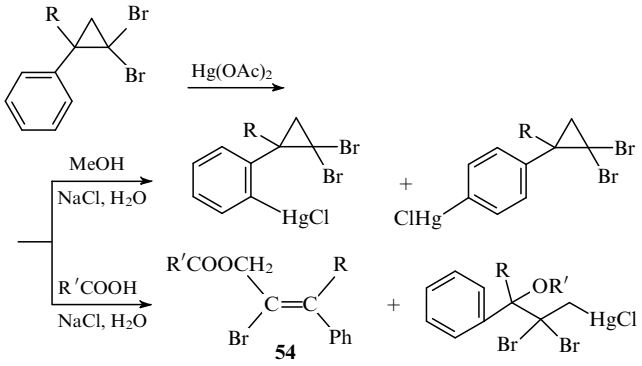
R = Pr^i, Bu^t.

The behaviour of 1,1-dichloro- and 1,1-dibromo-2-phenylcyclopropanes in conjugate mercuration reactions has also been investigated.[57] It was established that, on treatment of 1,1-dichloro-2-phenyl- and 1,1-dichloro-2-methyl-2-phenylcyclopropanes with mercury acetate in hydroxylated solvents, the aromatic ring is mercurated in the *ortho*- and *para*-positions, while the three-membered ring is not involved.



R = H, Me; R′ = Me, AcO, CHO.

1,1-Dibromo-2-phenylcyclopropane gives rise to an aromatic mercurio-derivative only in methanol.[57] In formic and acetic acids, the reactions of mercury acetate with 1,1-dibromo-2-phenyl- and 1,1-dibromo-2-methyl-2-phenylcyclopropanes proceed with the opening of the small ring. This process takes place stereo- and regio-specifically and leads to the alkenes **54** with the *Z*-configuration.



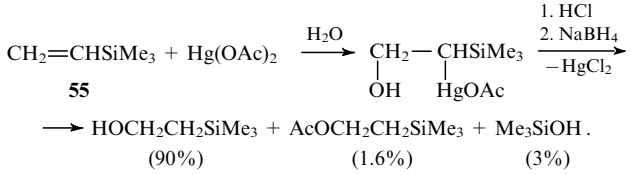
R = H, Me; R′ = H, Me.

IV. Addition of mercury salts to a C = C bond

One of the most important and general methods for the formation of a carbon–mercury bond is mercuration,[1–7] which can be regarded as electrophilic interaction of mercury-containing cations with electron-excess systems.

Among the methods for the synthesis of OMC, the reactions involving the addition of mercury salts to the multiple bonds in alkenes and ethynes in the presence of various nucleophiles are of special importance. An enormous number of mercury compounds, which possess a series of unique properties, have been synthesised by this method.[3, 6] These substances are remarkable because they exhibit strikingly a dual reactivity, like tautomeric compounds. In some cases, they react as true organometallic substances, whilst in others they behave like π-complex adducts of the mercury salt with an unsaturated compound as an addend, which can be substituted as a whole.[3] Apparently, the vigorous development of methods of synthesis of OMC has continued because of these extremely interesting properties.[7] During the last decade, attention has been concentrated on various aspects of the conjugate mercuration of unsaturated compounds.

Thus the hydroxymercuration of silicon-containing alkenes — trimethyl-vinylsilane **55** and allyltrimethylsilane **56** — with mercury acetate in the 1 : 1 water–THF mixture has been studied.[58] The demercuration of the resulting hydroxymercurioacetate by the initial treatment with an alkaline solution of $NaBH_4$ and then with HCl leads to a complex mixture of reaction products.



The hydroxymercuration of the alkene **55** with mercury acetate in a D_2O-THF-d_8 mixture affords only 2-acetoxymercurio-1-deuterioxy-2-trimethylsilylethane (**57**) and, when CD_3COOD is used as the solvent, 2-acetoxymercurio-1-deuterioacetoxy-2-trimethylsilylethane (**58**) is formed.[58]

$DOCH_2CH(HgOAc)SiMe_3$ (**57**) $\qquad$ $CD_3COOCH_2CH(HgOAc)SiMe_3$ (**58**)

The hydroxymercuration of the allyl derivative **56** under the same conditions with subsequent demercuration of the resulting intermediate mercury-containing derivative also affords a mixture of products.[58]

$$CH_2{=}CHCH_2SiMe_3 \xrightarrow[2.\ NaBH_4]{1.\ Hg(OAc)_2} \underset{\mathbf{56}}{} CH_2{=}CHMe + PrOH + Pr^iOH + Me_3SiOH + (Me_3Si)_2O$$

$$\mathbf{56} \xrightarrow[AcOH,\ 20\ ^\circ C]{Hg(OAc)_2} CH_2{=}CHCH_2HgOAc \quad (\mathbf{59})$$

$$\mathbf{59} \xrightarrow[2.\ CD_3COOD]{1.\ Hg(OAc)_2} AcOHgCH_2CH(OAc)CH_2HgOAc \quad (\mathbf{60})$$

$$\mathbf{59} \xrightarrow[D_2O-THF\text{-}d_8]{Hg(OAc)_2} AcOHgCH_2CH(OD)CH_2HgOAc \quad (\mathbf{61}) \xrightarrow[2.\ H^+]{1.\ NaBH_4} Pr^iOH$$

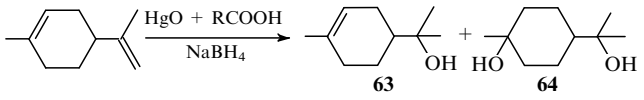
The interaction of the alkene **56** with mercury acetate in glacial acetic acid at room temperature leads to allyl mercurioacetate **59**, the reaction of which with $Hg(OAc)_2$ in CD_3COOD affords the demercurated compound **60**. The hydroxymercuration of compound **59** in a D_2O-THF-d_8 mixture leads only to the product **61**, which is converted into isopropyl alcohol on demercuration.[58]

A method for the selective hydroxymercuration of alkenes by mercury salts, formed *in situ* from HgO and carboxylic acids under the influence of ultrasound, has been described.[59] Thus the interaction of oct-1-ene with HgO and RCOOH in proportions of 1 : 1 : 2 in aqueous THF leads to compound **62**, which affords a 85% yield of 2-octanol on reduction with $NaBH_4$.

$$C_6H_{13}CH{=}CH_2 \xrightarrow[RCOOH]{HgO} \underset{\mathbf{62}}{C_6H_{13}CH(OH)CH_2HgOCOR} \xrightarrow[2.H^+]{1.NaBF_4} C_6H_{13}{-}CH(OH){-}CH_3$$

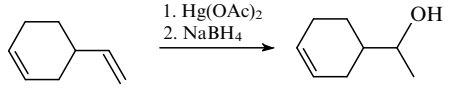
R = Me, Bu^t, C_9H_{19}, CBr_3, Pr, Ph.

The hydroxymercuration of limonene leads, after reduction, to a mixture of the alcohols **63** and **64**, the ratio of which depends on the reaction conditions.[59]



63 **64**

The highest yield (80%) of α-terpineol **63** is observed in Bu^{t}OH as the solvent, using $C_{17}F_{15}COOH$, and an exposure to ultrasound for 7 min. When the analogous reaction with 4-vinylcyclohexene was carried out in the presence of $Hg(OAc)_2$, the yield of 1-(cyclohex-3-enyl)ethanol (**65**) did not exceed 20%, while in the presence of PrCOOH and HgO with exposure to ultrasound for 2 h the yield of the alcohol **65** was 67% with 100% selectivity.[59]



65

The biomimetic asymmetric hydroxymercuration of alkenes, catalysed by β-cyclodextrin, has been achieved.[60]

$$ArCH{=}CHR \xrightarrow[2.\ Hg(OAc)_2]{1.\ \beta\text{-cyclodextrin}} ArCH(OH)CHR-HgOAc$$

Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4;

R = H, CH_2OH, COOH, COOMe, COOEt, $COOPr^i$.

The asymmetric solvomercuration of alkenes has been carried out[61] in chiral micellar systems with addition to the reaction mixture of the optically active salts PhCH(OH). .$CHMeN^+Me_2C_{12}H_{25}\,Br^-$ or $PhCH(OH)CHMeN^+Me_2$. .$C_{16}H_{33}\,Br^-$.

Compounds **66** were obtained as a result.

$$RCH{=}CH_2 + Hg(OAc)_2 \xrightarrow{H_2O} \underset{\mathbf{66}}{RCH(OH)CH_2HgOAc}$$

R = Ph, Bu^n, $Me(CH_2)_4CH(OH)$.

The interaction of styrene derivatives **67** with mercury acetate in methanol at 25 °C leads to the methoxymercuration products **68**, the reduction of which with $NaBH_4$ in MeOH gives rise to the corresponding methyl ethers.[62]

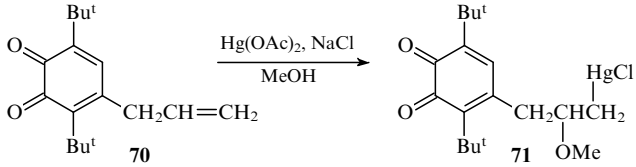
$$\underset{\mathbf{67}}{PhR^1C{=}CR^2R^3} \xrightarrow[MeOH]{Hg(OAc)_2} PhC(R^1)(HgOAc){-}CR^2R^3\ (OMe)\ (\mathbf{68}) \xrightarrow{NaBH_4,\ MeOH} PhR^1C(OMe){-}CHR^2R^3$$

R^1, R^2, R^3 = H, Me.

Allylbenzene reacts with mercury acetate under analogous conditions. subsequent demercuration of compound **69** leads to 2-methoxy-1-phenylpropane.[62]

$$PhCH_2CH{=}CH_2 \xrightarrow[MeOH]{Hg(OAc)_2} PhCH_2CH(OMe){-}CH_2HgOAc\ (\mathbf{69}) \xrightarrow[MeOH]{NaBH_4} PhCH_2CH(OMe)Me.$$

The presence of the allyl group in the molecule of the quinone **70** made it possible to carry out the conjugate mercuration reaction with mercury acetate in methanol,[63] which led to the formation of the organomercury compound **71**.



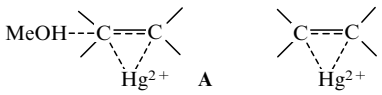
70 **71**

The mechanism of the mercuration of the C = C bond has been investigated[64] in relation to the methoxymercuration of ethene by mercury acetate in MeOH and the hydroxymercuration of 2-methylpropene by mercury perchlorate in water.

$$H_2C{=}CH_2 + Hg(OAc)_2 \xrightarrow{MeOH} \underset{\mathbf{72}}{MeOCH_2CH_2HgOAc},$$

$$Me_2C{=}CH_2 + Hg(ClO_4)_2 \xrightarrow{H_2O} \underset{\mathbf{73}}{Me_2C(OH)CH_2HgClO_4}.$$

It was established that both reactions take place stereoselectively and that the addition of mercury to the C = C bonds proceeds *via* the formation of the intermediate **A** and its elimination proceeds *via* the intermediate **B**.



The protolysis of compound **72** is accompanied by the formation of the initial ethene, whilst the protolysis of

$HOCH_2CH_2HgClO_4$ is accompanied by hydride transfer with formation of acetaldehyde.[64]

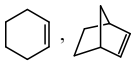
$$HOCH_2CH_2HgClO_4 \xrightarrow{HClO_4} MeCHO + Hg(ClO_4)_2 + H_2.$$

The protolysis of compound **73** in the presence of carboxylic acid salts leads to Bu^tOH.[64]

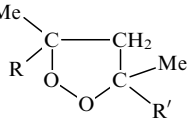
The nitratomercuration of a series of alkenes *via* the addition of mercury nitrate to the latter in methylene chloride at 0 °C has been achieved.[65] The reactions take place stereospecifically and, depending on the structures of the groups R and R′, the *trans*- or *cis*-adducts **74a–c** are formed in ~100% yield. On treatment of the freshly prepared adducts **74** with bromine at 0 °C, $HgNO_3$ is substituted by the halogen.[65]

$$RCH{=}CHR' \xrightarrow{Hg(NO_3)_2} \underset{\mathbf{74a-d}}{RCH(ONO_2)CHR'(HgONO_2)} \xrightarrow{Br_2} RCH(ONO_2)CHR'Br$$

R = Bu, R′ = H (**a**); R = C_6H_{11}, R′ = H (**b**); R = R′ = Et (**c**);

R, R′ =  (**d**).

The interaction of nonconjugated dienes **75** with mercury nitrate and 80% hydrogen peroxide in CH_2Cl_2 at 20 °C followed by treatment with KCl or KBr leads to unstable mercurated hydroperoxides **76**, which are readily reduced by $NaBH_4$ to the cyclic peroxides **77a–c** in 64%–77% yields.[66]

$$\underset{\mathbf{75a-c}}{CH_2{=}CR{-}CH_2{-}CR'{=}CH_2} \xrightarrow[KCl]{Hg(NO_3)_2,\ H_2O_2} \left[\begin{array}{l} OOH \quad\quad OOH \\ CH_2{-}CR{-}CH_2{-}CR'{-}CH_2 \\ HgCl \quad\quad\quad HgCl \end{array}\right] \xrightarrow{NaBH_4} \underset{\mathbf{77a-c}}{\text{}}$$

76a–c

R = R′ = H (**a**); R = R′ = Me (**b**); R = H, R′ = Me (**c**).

The monoalkenes **78a–j** interact with an equimolar amount of mercury acetate in 30% aqueous H_2O_2 and are converted on subsequent treatment with KBr into the mercurated hydroperoxides **79a–j** and the alcohols **80a–j**.[67,68]

$$\underset{\mathbf{78a-j}}{R^1R^2C{=}CHR^3} + Hg(OAc)_2 \xrightarrow{H_2O_2,\ KBr} \underset{\mathbf{79a-j}}{R^1R^2C(OOH)CHR^3HgBr} + \underset{\mathbf{80a-j}}{R^1R^2C(OH)CHR^3HgBr}$$

$$\downarrow NaBH_4$$

$$\underset{\mathbf{81a-j}}{R^1R^2C(OOH)CH_2R^3}$$

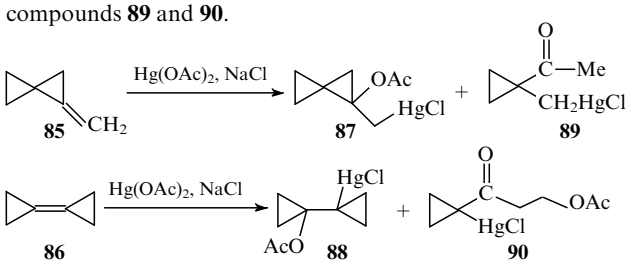
$R^2 = R^3 = H$: R^1 = Ph (**a**), 2-MeC_6H_4, (**b**), 4-MeC_6H_4, (**c**), 4-$MeOC_6H_4$, (**d**), Bu, (**e**);

R^1 = Ph, R^2 = Me, R^3 = H (**f**); R^1 = H, $R^2 + R^3 = (CH_2)_4$ (**j**).

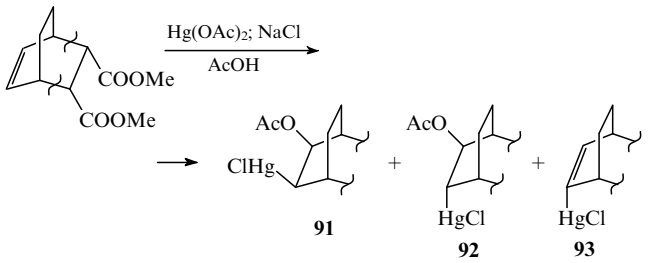
The yields of compounds **79** and **80** and their ratio depend on the nature of the alkene **78**. Thus the arylaIkenes **78a–d** or the geminally substituted alkenes **78f** form only the corresponding hydroperoxides **79** in ~90% yield. Monoalkyl- or 1,2-dialkylalkenes afford mixtures of compounds **79** and **80** in low yields.[67] The reductive demercuration of compound **79** with sodium tetrahydroborate results in the formation of the alkylhydroperoxides **81a–j**[68] and not cyclic peroxides as in the case of compounds **77**. In contrast to the alkenes **78**, the interaction of (*Z*)- or (*E*)-but-2-ene with $Hg(OAc)_2$ in 30% H_2O_2 leads to the more complex mixture of reaction products **82–84**.[67]

$$MeHC{=}CHMe + Hg(OAc)_2 \xrightarrow{H_2O_2} \underset{\mathbf{82}}{HMe_2CHgOAc} + \underset{\mathbf{83}}{HMeC(OH){-}CHMeHgOAc} + \underset{\mathbf{84}}{HCOOH}.$$

The reaction involving the acetoxymercuration of isomeric methylenecyclopropanes (methylenespiropentane **85** and bicyclopropylidene **86**) has been investigated.[69] The main reaction path is the formation of the adducts **87** and **88** respectively at the double bonds with retention of the three-membered ring. However, this is accompanied, albeit to only a slight extent, by the competitive addition to the C–C bond of cyclopropane with formation of compounds **89** and **90**.

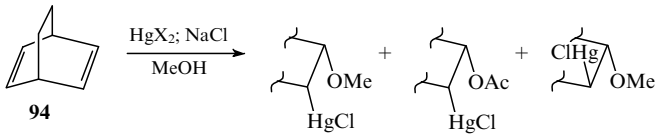


The stereoselectivity of the reaction of mercury acetate with dimethylbicyclo[2.2.2]oct-5-ene-2,3-*cis*-*endo*-dicarboxylate in acetic acid has been studied.[70] Several reaction products (compounds **91**, **92**, and **93**) were isolated in proportions of 11 : 4 : 5 respectively.



The formation of the unsaturated organomercury compound **93** in this reaction is due to the characteristic features of the structure of the intermediate, which in reactions of this type has the structure of a β-mercury-substituted carbonium ion.[70] The results obtained indicate severe steric requirements for the approach of the mercurating agent to the double bond of the initial compound while the coordination interaction of the carboxylate groups and the mercury atom plays a less significant role in this instance.[70]

It has been established by ^1H, ^{13}C, and ^{199}Hg NMR method [71] that, in the interaction of mercury salts with bicyclo[2.2.2]octa-2,5-diene **94** in methanol, the main reaction path involves the formation of products with the *endo*-disposition of the mercury atom (the ratio of the adducts is 34 : 58 : 8).

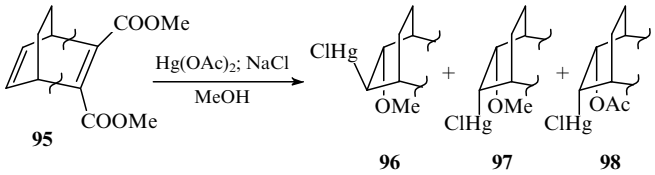


X = Cl, OAc.

The regioselectivity and stereospecificity of the reactions of mercury salts with dimethylbicyclo[2.2.2]octa-2,5-diene-2,3-dicarboxylate (**95**) in various solvents have also been investigated.[72] The reagents employed were mercury acetate in MeOH or AcOH, mercury nitrate, and the $Hg(OAc)_2$–NaN_3 (1 : 3) system in methanol. The products were isolated after treating the reaction mixture with an aqueous solution of NaCl.

In contrast to the mercuration of the diene **94**,[71] in the mercuration of the diene **95** with mercury acetate and nitrate in methanol the dominant path becomes the formation of the *trans*-solvatoadduct **96** with the *exo*-disposition of the Hg atom.[72]

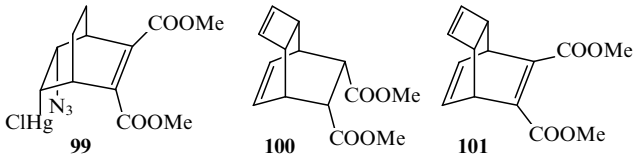
Compounds **96**, **97**, and **98** in proportions of 66 : 21 : 13 are formed in the reaction with mercury acetate.[72]



95 **96** **97** **98**

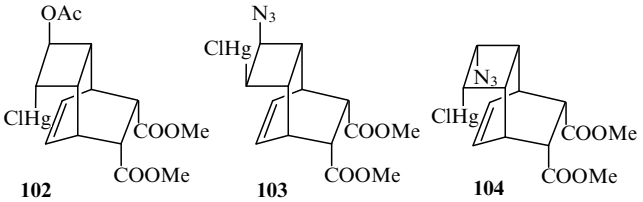
The use of mercury nitrate as the reactant leads to the solvatoadducts **96** and **97**, the content of compound **96** in the reaction mixture increasing to 77%.[72] When the reaction with mercury acetate is carried out in AcOH or with the $Hg(OAc)_2 - NaN_3$ system in methanol, the *endo*-products **98** and **99** are mainly formed in ~70% yield.

The regioselectivity and stereochemistry of the mercuration of the tricyclic diene **100** and triene **101** by a mixture of $Hg(OAc)_2$ and NaN_3 followed by the addition of NaCl to the reaction mixture have been investigated in a series of studies.[73–81]



99 **100** **101**

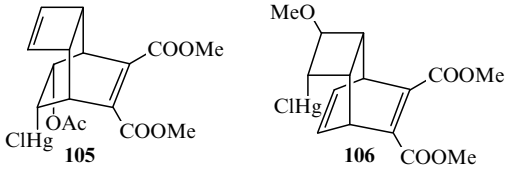
It was established that[73] the interaction of the diene **100** with mercury acetate in acetic acid results in the formation of the *trans*-solvatoadduct **102** with the *endo*-disposition of the mercury atom.



102 **103** **104**

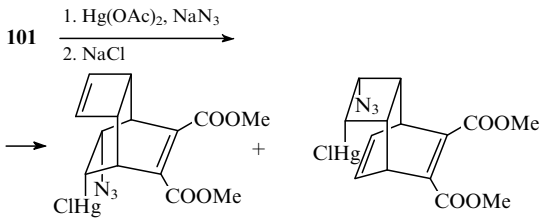
Different stereochemistry and regiochemistry were observed in the reaction of the diene **100** with the $Hg(OAc)_2 - NaN_3$ mixture. Depending on the reactant ratio, only the *exo*-(*cis*-adduct) **103** (for the ratios 1 : 1 : 3) or a mixture of the *exo*-(*cis*-adduct) **103** and the *endo*-(*cis*-adduct) **104** (for the ratios 1 : 1 : 1) is formed,[74–76] with the isomer **103** predominating.

When the reaction of the triene **101** is carried out in acetic acid, the mercury salt adds preferentially to the double bond of the cyclohexadiene fragment with formation of the *endo*-(*cis*-adduct) **105**. However, in methanol the double bond of the four-membered ring is involved in the reaction with mercury nitrate and *endo*-(*trans*-isomer) **106** is formed as the main product.[77,78]



105 **106**

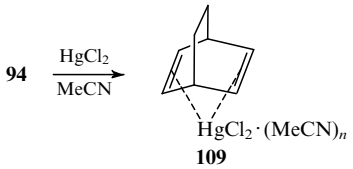
The study of the regiochemistry and stereochemistry of the azidomercuration of the triene **101** showed that the double bond of the cyclohexadiene fragment is involved preferentially in the reaction with formation of the *endo*-(*cis*-adduct) **107**; the attack on the four-membered ring proceeds from the sterically less accessible side and also involves the formation of the *endo*-(*cis*-isomer) **108**.[79]



107 **108**

Such unusual regiochemistry in the conjugate mercuration of the diene **100** and the triene **101** may be due to the coordination interaction between the mercury salt and the sterically close double bonds[80] or, in more general terms, between the mercury salt and suitable functional groups of the substrate.[81]

This has been recently confirmed by a study[82] in which the possibility of the formation of a complex in the $HgCl_2$–bicyclo[2.2.2]octa-2,5-diene **94** system in acetonitrile was investigated by ^{199}Hg NMR. It was established that, for a series of solutions with a constant concentration of the mercury salt and a variable concentration of the diene, a pronounced downfield shift of the ^{199}Hg resonance signal is observed, which indicates the formation of a complex, probably having the structure **109**.

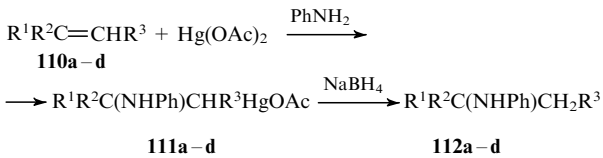


109

[**94**]/[$HgCl_2$]	1.25	1.5	2.0	2.5	3.0	5.0
$\Delta\delta(^{199}Hg)$ /ppm	11.88	14.85	18.20	21.80	25.61	43.56

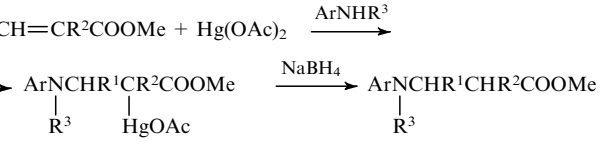
On the basis of the data obtained and using the conditions for the validity of the $\delta(^{199}Hg)^{-1}$–[**94**] linear equation,[83,84] the complex formation constant K_f and the relative chemical shift in the ^{199}Hg NMR spectrum for complex **109** were found by the method of least squares.[82] These quantities proved to be 0.55–0.08 and 186±26 ppm respectively.

Apart from the azidomercuration reactions leading to the simultaneous formation of C–Hg and C–N bonds, aminomercuration, reactions, which result in the formation of bonds of the same type, have been described.[85,86] The conditions for the direct amination of the alkenes **110a–d** by treatment with aniline and mercury acetate in an aqueous medium with the intermediate formation of the aminomercuration products **111a–d** have been elucidated.[85] Subsequent reduction of compounds **111** with $NaBH_4$ in an alkaline medium leads to the amines **112a–d**.



$R^1 = R^2 = R^3 = H$ (**a**); $R^1 = Me$, $R^2 = R^3 = H$ (**b**);
$R^1 = R^2 = Me$, $R^3 = H$ (**c**); $R^1 = R^2 = R^3 = Me$ (**d**).

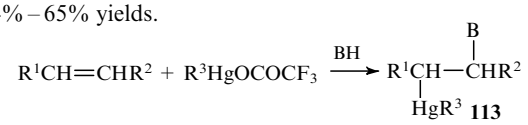
The reactions of the methyl esters of unsaturated acids with $Hg(OAc)_2$ and ArNHR led to the synthesis of the corresponding α-mercurated esters, which were then reduced with $NaBH_4$ in an alkaline medium to the methyl esters of the corresponding β-aminoacids.[86]



$R^1 = R^2 = H$; $R^1 = R^2 = Me$; Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4; $R^3 = H$, Me.

Organomercury reagents, which had been rarely used previously [3, 6, 7] for the conjugate mercuration of alkenes, have been employed for this purpose in recent years.[87, 88] Nevertheless, these reactions should be regarded as a convenient method of synthesis of asymmetric OMC.

The mercuration of styrene and cyclohexene by polyfluoroalkylmercury salts with participation of MeOH and $HNMe_2$ as nucleophiles has been investigated.[87] It was established that conjugate addition takes place in accordance with the Markovnikov rule with formation of the asymmetric OMC **113** in 24% – 65% yields.



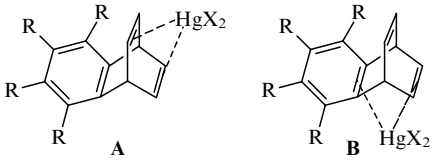
$R^1 = H$, $R^2 = Ph$; $R^1 + R^2 = (CH_2)_4$; $R^3 = CF_3$, C_3F_7; $B = OMe$, NMe_2.

In the case of perfluoropropene in the presence of caesium fluoride in DMF, asymmetric fully substituted OMC with a perfluorinated substituent were obtained.[88]



$R = Ph$, C_6Me_5, $Ph_2C{=}CH$, 1,2,4,5-$Me_4C_6HgOCOCF_3$.

New aspects of the addition of mercury salts to a C = C double bond in various substrates have been investigated in a recently published series of studies.[43, 89–93] In particular, the regiochemistry and stereochemistry of the reaction involving the addition of mercury salts to benzobarrelene and tetrafluorobenzobarrelene in acetic acid and methanol have been investigated [43] and the influence of the structure of the substrate on the regiochemistry of the reaction has been examined. It follows from the data obtained [43] that the reaction products are formed as a result of the attack by the mercury salt on the double bond of the cyclohexadiene fragment both from the side of the arene ring and from the side of the bridging ethylene group. It is postulated here that the regiochemistry of the mercuration reaction is determined by the 'reagent – substrate' interaction and, in relation to the dienes indicated above, it may occur in two ways: the reagent – two double bonds of the cyclohexadiene fragments (**A**) and the reagent – double bond of the cyclohexadiene fragment – benzene ring (**B**).



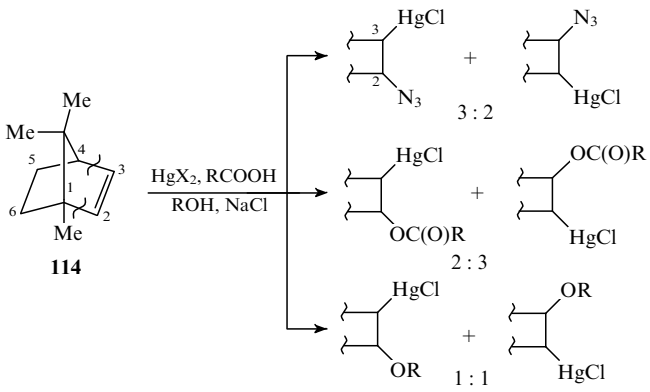
A **B**

R = H, F; X = OAc, N_3.

According to the authors,[43] the preferential formation of the transition state **A** is characteristic of the reactions investigated. This suggests that the system of two skeletal double bonds exhibits more marked chelating properties relative to the mercury atom than the double bond – arene fragment system.

It has been established [89] that the regiochemistry of the mercuration reaction of bornylene **114** depends on the nature of the mercurating agent and the solvent.

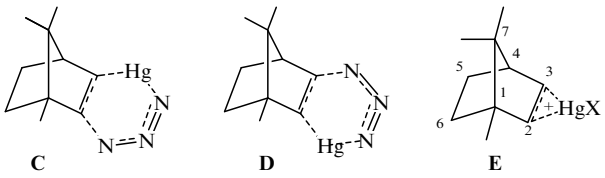
It is important to note that the ratio of the regioisomeric adducts in the reaction of bornylene **114** with mercury azide is reversed when bornylene interacts with mercury acetate. According to Sokolova *et al.*,[89] this is due to the occurrence of the reactions *via* different mechanisms. The regiochemical data provide grounds for the hypothesis that mercury azide adds to bornylene **114** in accordance with a concerted mechanism *via* the transition states **C** and **D**. The transition state **C** is preferred in view of the smaller steric hindrance.



114

X = OAc, OCOEt, N_3; R = Me, Et.

On the basis of the ratio of the regioisomers in the reaction of bornylene **114** with mercury acetate in alcohols and acetic acid, Sokolova *et al.*[89] suggested that the mercurenium intermediate **E** is formed in the reactions with mercury acetate and propionate and is then converted into the above reaction products.

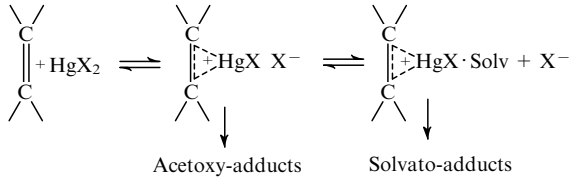


C **D** **E**

X = OAc, OCOEt.

The preferential formation of the reaction products as a result of attack by the nucleophile on the 3-position, for which the steric factor is less important, is possible precisely for this mechanism.

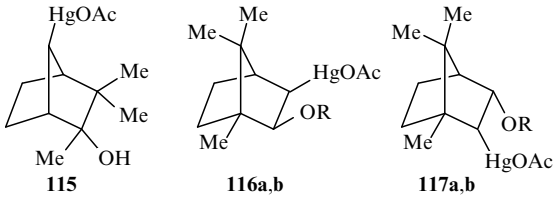
The kinetics of the mercuration of bornylene [90] and cyclohexene [91] have been investigated in various solvents (H_2O – MeCN, MeOH, EtOH, PrOH, AcOH) in the presence of sodium acetate and lithium perchlorate. The introduction of NaOAc into the mixture reduces sharply the rate of addition of mercury acetate to compound **114** and cyclohexene in alcohols. The formation of acetoxy-adducts then becomes the main path in the mercuration of compound **114** while the content of solvato-adducts falls from 76% (in the absence of NaOAc) to 19% (in 4×10^{-4} M NaOAc).[91] A reaction mechanism with participation of ion pairs and a solvated mercurenium ion as intermediates has been proposed [90, 91] and confirmed by the method of stationary concentrations.



Acetoxy-adducts Solvato-adducts

According to Kartashov *et al.*,[91] the influence of NaOAc on the rate of formation of the reaction products is manifested *via* the common ion effect (X = OAc).

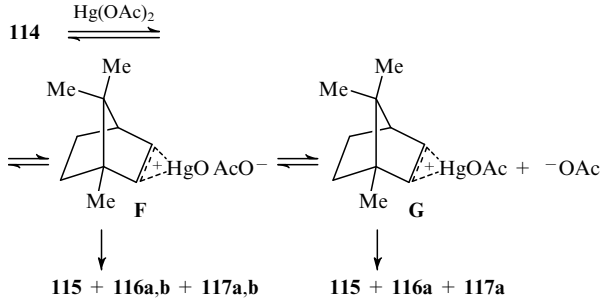
The reaction of mercury acetate with bornylene **114** has been investigated [92] in the THF – H_2O and MeCN – H_2O mixed solvents (75:25 by volume) and the influence of the addition of NaOAc on the rate of reaction and the composition of the products was studied. It was established that the addition of NaOAc to the MeCN – H_2O mixture diminishes the amount of the rearranged product **115** and alters radically the ratio of the regioisomeric solvato-adducts **116a**,**b** and **117a**,**b**, stimulating the formation of the products of the addition of $Hg(OAc)_2$ to the bornylene double bond.



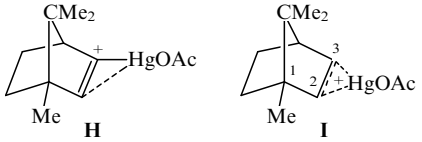
115 **116a,b** **117a,b**

R = H (**a**), Ac (**b**).

It is believed[92] that the reaction of mercury acetate with bornylene **114** proceeds with participation of the ion pair **F** and the free mercurenium ion **G**, but these intermediates have different structures.

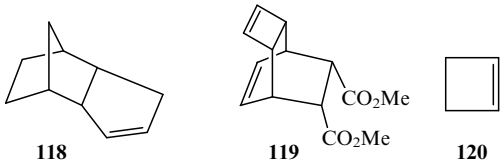


The considerable amount of the rearranged product **115** and the preferential formation of the solvato-adduct **116a** (in the absence of added NaOAc) give grounds for the assumption that the mercurenium ion **G** has the asymmetric structure **H**.[92] When NaOAc is added, whereupon the reaction proceeds *via* the ion pair **F**, the preferential formation of the solvato-adduct **117a** and the appreciable inhibition of the Wagner–Meerwein rearrangement, leading to the product **115**, can apparently be explained by the more symmetrical structure of the cationic fragment **I** in the ion pair **F**.



The steric hindrance generated by the methyl group in the 1-position of the intermediate **I** to the approach of the nucleophile (OR) promotes the addition of the nucleophile ($^-$OR) to the more accessible C(3) atom with the preferential formation of the product **117a**.[92]

The kinetics of the addition of $Hg(OAc)_2$ to strained and unstrained alkenes have been investigated in MeOH in the presence of NaOAc.[93] The phenomenon of the salt effect led to the conclusion that, in the reactions with unstrained alkenes derived from allyl, cyclopentene, and cyclohexene, the reactant is the $^+$HgOAc ion. In the case of strained alkenes such as compounds **118**–**120**, the reactant is $Hg(OAc)_2$.



118 **119** **120**

On the basis of these investigations, the mechanisms of the reaction involving the solvatomercuration of alkenes having different structures have been proposed.[93]

The reactions involving the addition of a new mercury salt — mercury dinitroamidate (MDNA) **121** — to alkenes such as ethene, propene, *cis*- and *trans*-but-2-enes, and norbornene have been studied recently.[94] In most cases, water, methanol, and diethyl ether were used as the solvent.

When ethene is passed into an aqueous MDNA solution for 5 h, the mercury-containing derivative of diethyl ether is precipitated in 51% yield.

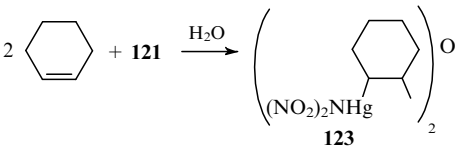
$$2H_2C{=}CH_2 + 2Hg[N(NO_2)_2]_2 + H_2O \xrightarrow[\mathbf{121}]{} O[CH_2CH_2HgN(NO_2)_2]_2 + 2HN(NO_2)_2.$$

When an aqueous solution of MDNA is acted upon by propene, a product with an unknown structure, soluble in water and the usual organic solvents, is precipitated.

The addition of MDNA to *cis*- and *trans*-butenes in water leads, as in the case of ethene, to the corresponding dimercurated ethers **122** and, depending on the structure of the alkenes, different adducts are formed, which the authors[94] believe to be the *threo*- and *erythro*-isomers.

$$2MeCH{=}CHMe + \mathbf{121} \xrightarrow{H_2O} \underset{\mathbf{122}}{O[CHMeCHMeHgN(NO_2)_2]_2}.$$

The product of the addition of MDNA to cyclohexene in water is also, according to IR spectroscopic data, a mercurio-derivative of the corresponding ether **123**.[94]



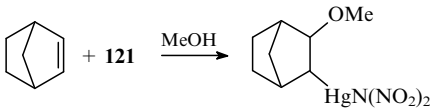
It was found that, when MeOH is used in the above reactions, the competition for the intermediate mercurenium cation is won not by $^-$OMe but by $^-N(NO_2)_2$.[94] As a result, *N*,*N*-dinitro-β-dinitramidemercurioethylamine is formed in 95% yield and the product of the conjugate methoxymercuration — 1-methoxy-2-dinitramidemercurioethane is formed in only 5% yield as a result of the interaction of ethene with MDNA in methanol.

$$H_2C{=}CH_2 + \mathbf{121} \xrightarrow{MeOH} \underset{(95\%)}{(NO_2)_2NHgCH_2CH_2N(NO_2)_2} + \underset{(5\%)}{(NO_2)_2NHgCH_2CH_2OMe}.$$

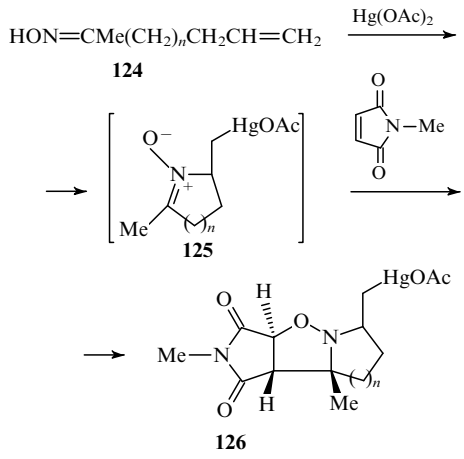
The conjugate mercuration involving the use of MDNA is extremely sensitive not only to the nature of the solvent but also to the structure of the alkene.[94] Thus the ratio of the products of the addition of MDNA to alkenes in methanol changes significantly on passing from ethene to its alkyl derivatives. According to ^{1}H NMR spectroscopic data, in the case of propenes the methoxymercuration products predominate over the corresponding *N*,*N*-dinitraminomercuration products, while in the case of but-2-enes only the methoxymercuration products are formed.

$$MeCH{=}CHMe + \mathbf{121} \xrightarrow{MeOH} MeOCHMeCHMeHgN(NO_2)_2.$$

The addition of MDNA to norbornene in MeOH takes place with formation of only the methoxymercuration product having the *exo*-(*cis*-structure).[94]

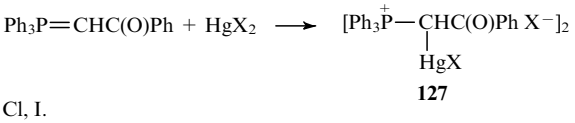


As a result of the addition of $Hg(OAc)_2$ to the double bond in the oximes **124** containing γ- or δ-alkenyl substituents, the intermediate compounds cyclise to the corresponding cyclic nitrones **125**. The latter react *in situ* with *N*-methylmaleimide (THF, 60 °C), forming the mercurated cyclic adducts **126** as a mixture of the *endo*- and *exo*-isomers.[95]



$n = 1, 2.$

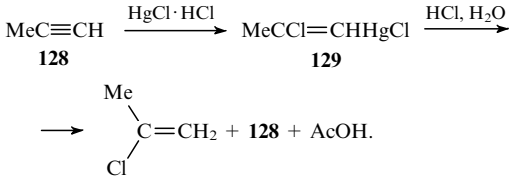
The addition of mercury salts HgX_2 to the C=P double bond present in stable triphenylphosphonium ylides led to the formation of the corresponding salt-like adducts **127**, which are dimeric according to X-ray diffraction data.[96]



X = Cl, I.

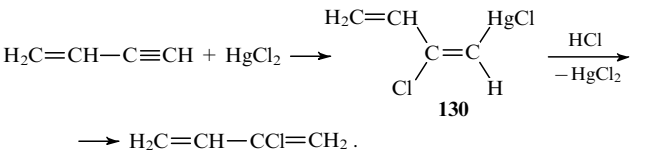
V. Addition of mercury salts to a C≡C bond

This is one of the most general and universal methods of synthesis of unsaturated organomercury substances, which are of considerable scientific interest, for example for the study of stereochemical problems in organometallic chemistry.[3,6] During the last 10–15 years, the studies on these lines have continued. Thus, the reaction of methylethyne **128** with the complex $HgCl_2 \cdot HCl$ has been investigated.[97] It was shown that the absorption of compound **128** at the freezing point of the $H_2O-HCl-HgCl_2$ system leads to (*E*)-1-chloromercurio-2-chloropropene **129**, which proved to be relatively unstable in air.



The reaction of compound **129** with a dilute hydrochloric acid solution leads to 2-chloropropene, the initial MeC≡CH, and acetic acid. The last compound is formed on hydration of MeC≡CH formed from compound **129** as a result of β-elimination.

The interaction of mercury(II) chloride with vinylethyne affords the *E*-1,2-adduct **130**.[97]

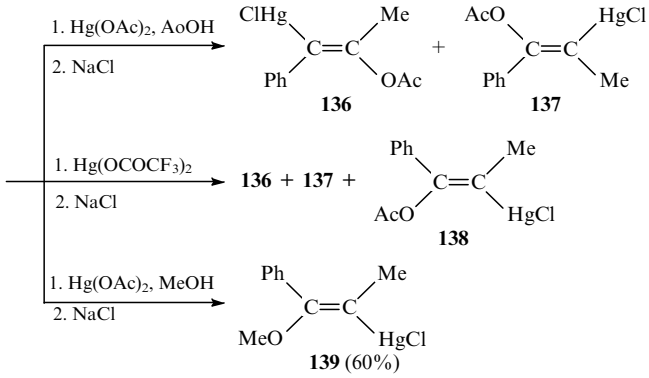


Compound **130** proved to be more stable than compound **129** during storage. However, on treatment with KI it decomposes with formation of the initial vinylethyne while treatment with HCl converts it into 2-chlorobuta-1,3-diene.[97]

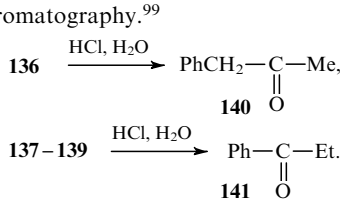
The conjugate alkoxymercuration of 2-methylbut-1-en-3-yne **131** by mercury acetate in various media has been studied.[98] A mixture of the products **132**–**134** is formed in alcohols, whilst in acid the sole product is compound **135** (Scheme 3).

The adducts **132**–**135** are readily reduced by $NaBH_4$ with formation of the corresponding unsaturated compounds.[98]

The *E*,*Z*-stereochemistry of the addition of mercury salts to acetylenic hydrocarbons has been studied in a series of investigations.[99–101] The reaction of methylphenylethyne with mercury acetate in acetic acid gives rise to a mixture of the isomers **136** and **137**, the reaction with mercury trifluoroacetate affords the three isomers **136**–**138** whilst that with $Hg(OAc)_2$ in methanol results in the formation of only one product — (*Z*)-2-chloromercurio-1-methoxy-1-phenylprop-1-ene (**139**).[99]

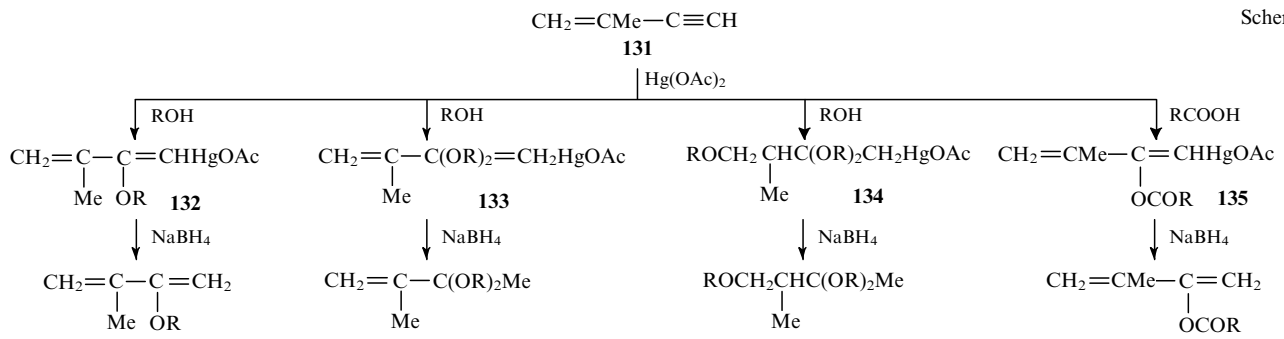


The protodemercuration of the alkene **136** in aqueous HCl solution yields the ketone **140**, whilst that of the alkenes **137**–**139** leads to the ketone **141**. The ketones were identified by gas–liquid chromatography.[99]



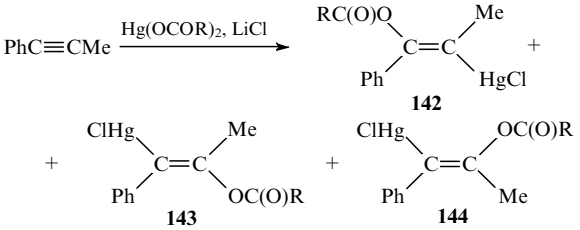
The study of the stereochemistry of the reaction of methylphenylethyne with $Hg(OCOR)_2$ in acetic and propionic acids showed[100] that the composition of the reaction product is

Scheme 3



R = Me, Et.

determined by the reactant ratio. When the reactant ratio is 2 : 1 (with R = Me), only the *E*-isomers **142** and **143** are formed in proportions of 3 : 2. For a reactant ratio of 1 : 1, the *Z*-isomer **144** is formed in addition to the reaction products **142** and **143** (in proportions of 86 : 8 : 6). When the ratio of the initial reactants is 1 : 2, the yield of the *Z*-isomer **144** increases and reaches 15%.

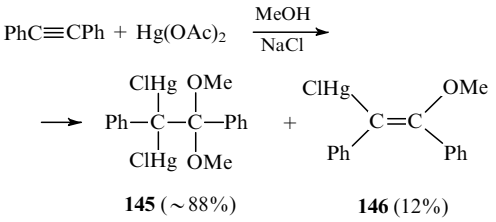


R = Me, Et.

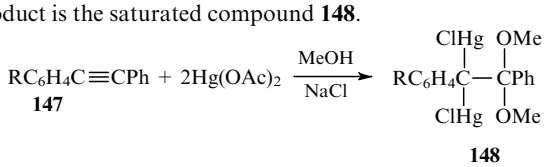
The reaction of diphenylethyne with mercury acetate in acetic acid leads only to the *E*-adduct ClHg–C(Ph)=C(Ph)–OAc.[101]

A study of the reactions of diphenylethyne with mercury salts in alcohols ROH (R = Me,Et, Pr^i) established [102, 103] that mercury acetate reacts with diphenylethyne in methanol and ethanol to form the corresponding (β-alkoxyvinyl)mercurio-adducts as a mixture of the *Z*- and *E*-isomers. Mercury trifluoroacetate reacts with diphenylethyne in ethanol and propan-2-ol with a high degree of stereoselectivity, forming the *Z*-isomers, the structure of which has been established by X-ray diffraction.

Contrary to the data of Bassetti *et al.*,[103] Kartashov *et al.*[104] established that the main product of the reaction of mercury acetate with diphenylethyne in methanol is a compound which contains no double bond, namely 1,1-di(chloromercurio)-2,2-dimethoxy-1,2-diphenylethane (**145**), which can be partly converted into (*Z*)-1-chloromercurio-2-methoxy-1,2-diphenylethene (**146**) under the reaction conditions (20 °C, 24 h).

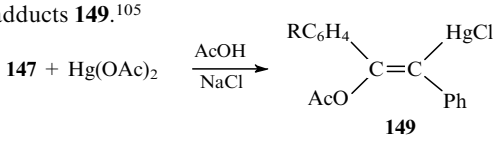


The reactions of arylphenylethynes **147** with mercury acetate in methanol and acetic acid have been studied.[105] The reaction in methanol has an unusual regiochemistry as a result of the addition of the electrophilic fragment $^+$HgOAc to the carbon atom to which the substituted phenyl group is attached. The reaction product is the saturated compound **148**.

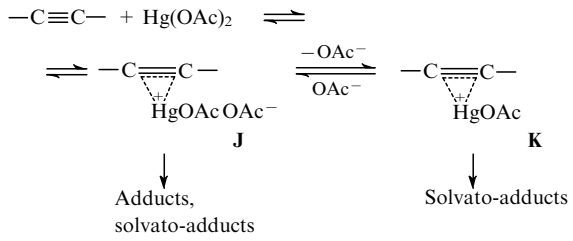


R = 4-Me, 4-OMe.

In acetic acid, the reaction proceeds with formation of the *E*-adducts **149**.[105]

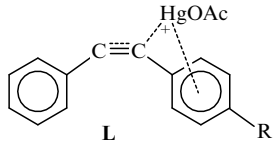


The kinetics of the reactions have also been investigated and the kinetic data have been analysed.[105] The influence of the addition of sodium acetate on the rate of formation and structure of the products **148** and **149** has been determined for the reaction in methanol. It was shown that the addition of NaOAc diminishes the rate of reaction, which becomes a minimum at a salt concentration of 3.0×10^{-3} M. For the reaction in acetic acid at the same NaOAc concentration, no decrease in rate was observed.[105] This can probably be accounted for by the charateristic features of the methoxymercuration of acetylenic compounds for which we believe that the same general mechanism of conjugate mercuration is valid as for alkenes,[91–93] examined in detail in the previous section.

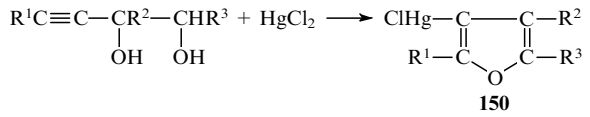


In acetic acid, the only intermediate is apparently the ion pair **J**, which dissociates in methanol to the an ion $^-$OAC and the cation **K**. In the case of the ion pair **J**, the triple bond is only slightly loosened and the positive charge is mainly concentrated on the mercury atom. In methanol, the ion pair **J** is converted into the cation **K** more rapidly than into the corresponding reaction products, but at the limiting sodium acetate concentrations the reaction probably proceeds preferentially *via* the ion pair **J** (as in acetic acid), which, being less reactive than the cation **K**, is converted more slowly into adducts and solvato-adducts.

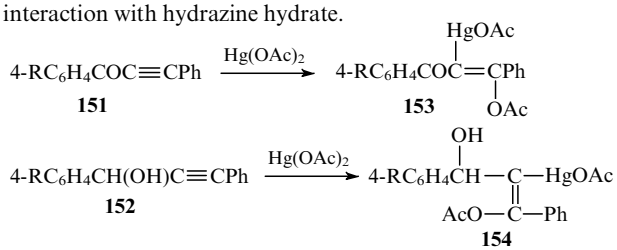
The unusual regiochemistry of compounds **148** can be explained by assuming that the free mercurenium ion **K** has an asymmetric structure, as in reactions with alkenes.[92] In this case, a complex may be formed between the electrophilic fragment of the intermediate **L** and the benzene ring with its higher electron density, the π-complex being subsequently converted into the products **148**.[105]



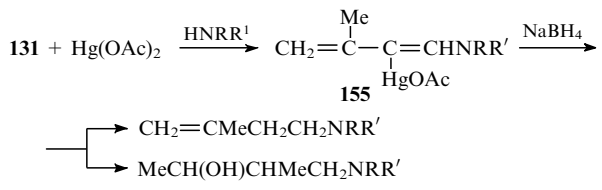
The interaction of equimolar amounts of 1,2-dialkylbut-3-yne-1,2-diols with mercury(II) chloride in alcohol leads to the corresponding derivatives of the mercurated furan **150** in high yields.[106]



Other reactions of functionally substituted ethynes with mercury salts are also of interest. Thus the interaction of the ketones **151** or alcohols **152** containing a triple bond, with mercury acetate in acetic acid leads [107] only to the *E*-adducts **153** and **154**, which afford the corresponding 5-(4-R-phenyl)-3-phenylpyrazoles on interaction with hydrazine hydrate.



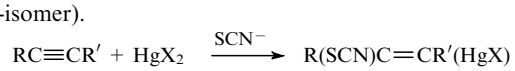
The addition of amines to compound **131** in the presence of mercury acetate has been investigated.[108] It has been suggested that the reaction results in conjugate aminomercuration of the enyne **131** with formation of conjugate organomercuriodienes **155**.



R = R′ = Me, Et; R + R′ = $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$.

The demercuration of the adducts **155** with $NaBH_4$ in an alkaline medium leads to alkenylamines and aminoalcohols [108] which are difficult to obtain by other methods.

The thiocyanatomercuration products **157** have been obtained by the interaction of ethyne and its derivatives **156** with mercury salts HgX_2 in the presence of the thiocyanate anion.[109,110] These compounds are formed regioselectively (in accordance with the Markovnikov rule) and stereospecifically (*E*-isomer).



R = R′ = H; R = Bu, R′ = H; R = OAc, R′ = H; R = R′ = Et;

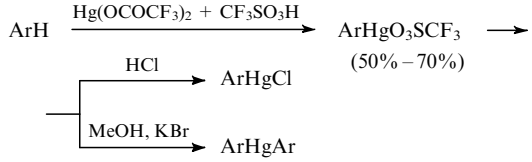
X = Cl, SCN.

The HgX group is readily substituted by hydrogen with retention of configuration on treatment of compound **157** with strong acids (H_2SO_4, HBF_4) and $NaBH_4$. It is also readily substituted by the halogens on treatment with iodine and bromine in pyridine or with $CuCl_2$ in acetonitrile.[109]

VI. Mercuration of aromatic compounds

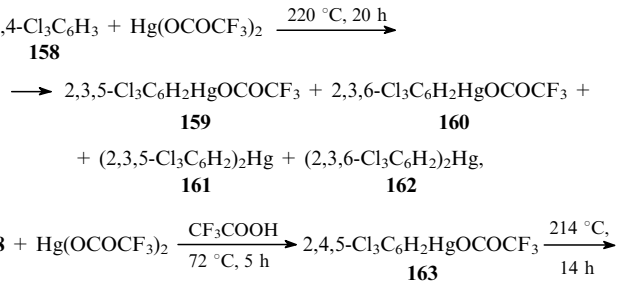
Many aromatic compounds (benzenoid and nonbenzenoid) are capable of entering into the mercuration reaction with divalent mercury salts, which leads to aryl-substituted OMC. The applicability of this reaction is very wide.

Many new examples of the mercuration reactions of aromatic compounds have been described during the last 15 years, which indicates that the studies on these lines are of current interest. Thus the mercuration of polyfluorobenzene derivatives with a mixture of mercury trifluoroacetate and fluorosulfonic acid in proportions of 1 : 2 has been achieved.[111]



Ar = C_6F_5, 4-MeC_6F_4, C_6F_4H, 3-$NO_2C_6F_4$, 3-BrC_6F_4, 4-HOC_6F_4, 4-$NH_2C_6F_4$, 3-$HOOCC_6F_4$, 4-$MeOC_6F_4$.

A mixture of organomercury polymers has been obtained by the mercuration of 1,2,4-trichlorobenzene (**158**) on heating with an excess of mercury trifluoroacetate. The individual OMC **159**–**162** were isolated from this mixture by extraction with benzene or xylene.[112]

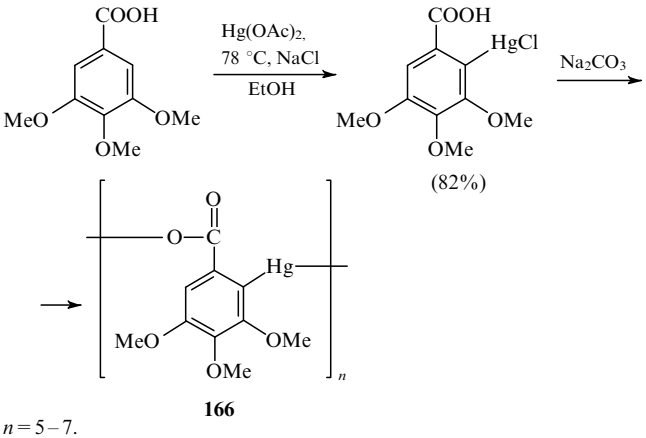


The position of the mercuriotrifluoroacetate group in compounds **159**–**162** was determined by their reaction with iodine. Treatment of compound **158** with mercury trifluoroacetate while refluxing in CF_3COOH leads to a regiospecific reaction, which results in the formation of compound **163**. On refluxing in an excess of the chloride **158**, compound **163** isomerises to compound **160** with its subsequent symmetrisation to compound **162**.[112] The structures of the above OMC were demonstrated by their independent synthesis *via* organolithium compounds or by the Nesmeyanov reaction.[112]

Other benzene derivatives (with both electron-donating and electron-accepting substituents) are readily mercurated on heating with a mixture of HgO and CF_3COOH forming the OMC **164** and **165**.[113] The mercuration reaction then obeys the usual rules [3,7] governing the direction of electrophilic substitution.

R = H, R′ = COOH; R = Me, R′ = COOH; R = Me, R′ = Cl.

3,4,5-Trimethoxybenzoic acid is also comparatively readily mercurated by mercury acetate with formation of 2-chloromercurio-3,4,5-trimethoxybenzoic acid, which is converted into the polymeric OMC **166** on treatment with sodium carbonate in acetone.[114]

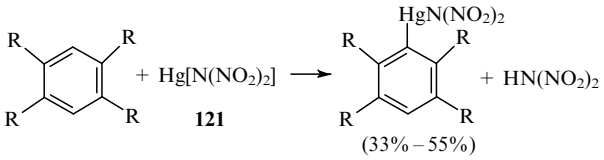


n = 5–7.

The interaction of benzene and its derivatives [115,116] with a mixture of mercury oxide and trichloroacetic acid on heating (60–70 °C) leads to 90%–100% yields of the corresponding mercuration products:

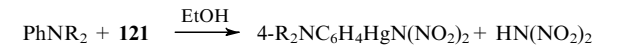
Ar = Ph, 4-MeC_6H_4.

The mercurating capacity of mercury dinitroamidate **121** in relation to a series of aromatic compounds has been investigated.[94] It was established that benzene is not mercurated by an ethereal solution of MDNA, since on prolonged refluxing of MDNA with benzene the decomposition of the mercury salt is faster than the mercuration reaction. However, refluxing of an aqueous solution of MDNA with benzene for 2 h leads to the product of monomercuration in the benzene ring (in 55% yield).[94] The more nucleophilic 1,2,4,5-tetramethylbenzene is readily mercurated on refluxing in a methanol solution of MDNA. This reaction proceeds even in ether at room temperature.[94]



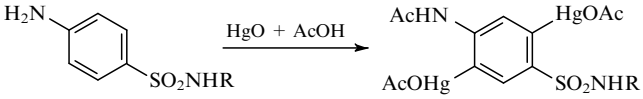
R = H, Me.

The mercuration of aniline in the *para*-position and of *N*,*N*-dimethylaniline with the aid of MDNA in alcoholic solution takes place very readily (in several minutes [94]).



R = H, Me.

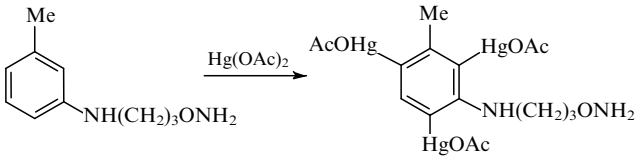
The mercuration of a large series of sulfanilamide preparations by heating them with HgO in acetic acid has been achieved.[117] Dimercurated compounds were then obtained.



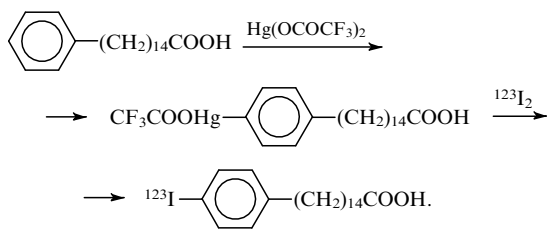
R = H, C(=NH)NH$_2$, , , .

3-Acetoxymercurio- and 3-chloromercurio-5-nitrosalicylaldehydes have been synthesised by mercurating 5-nitrosalicylaldehyde with mercury acetate.[118] It has been suggested that these OMC be used for the simultaneous introduction of mercury and pH-sensitive functional groups into proteins which do not contain thiol groups in order to investigate their structure.[118]

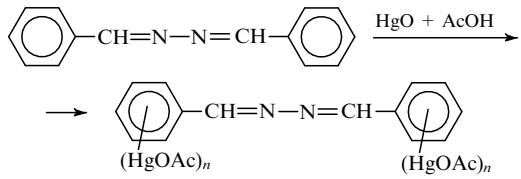
With the aim of synthesising mercury-containing reagents for the determination of carbonyl groups in biochemical research, *O*-substituted hydroxylamine, which makes it possible to introduce aminoxy-groups into proteins under mild conditions, was mercurated.[119]



In order to obtain radiopharmaceutical preparations labelled with radioactive iodine (^{123}I), 15-(4-iodophenyl)pentadecanoic acid was synthesised by mercurating 15-phenylpentadecanoic acid with mercury trifluoroacetate and subsequent treatment with radioactive iodine.[120]

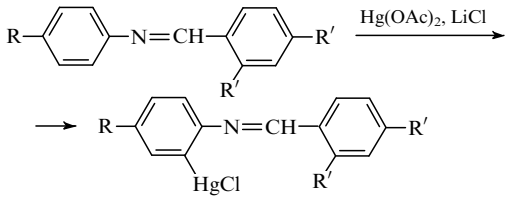


The mercuration of benzylideneazine with HgO in glacial acetic acid at 37 – 39 °C for 3 h leads to polymercurated compounds which are insoluble in many solvents and decompose at 200 °C without melting.[121]



n = 2 – 5.

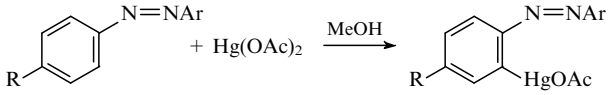
In contrast to this, arene azomethines interact with mercury acetate in alcohols (MeOH, EtOH) to form the corresponding products of *ortho*-mercuration in the *N*-substituted benzene ring in 80% – 92% yields.[122]



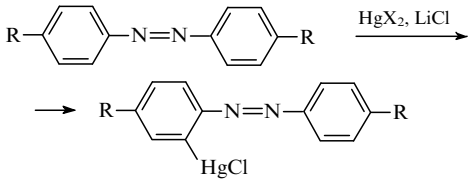
R = H, Me, OMe, Cl, Br, I; R′ = OMe, NO_2.

It follows from MINDO calculations of the regioselectivity of the mercuration of *N*-benzylideneaniline, *N*-benzylidene-2-toluidine, and 2-methoxy-*N*-(4-nitrobenzylidene)aniline that the electron density in the *N*-substituted benzene ring in the stable conformation is higher [123] and mercuration in this fragment takes place preferentially.[122]

The mercuration of aromatic azo-compounds by mercury acetate or trifluoroacetate on refluxing in methanol leads only to monomercurated compounds.[124, 125]

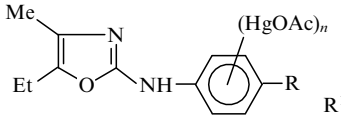


R = Me, NO_2, COOH;
Ar = 2,4-(HO)$_2$C$_6$H$_3$, 3,4,5-(HO)$_3$C$_6$H$_2$, α-C$_{10}$H$_7$, β-C$_{10}$H$_7$;

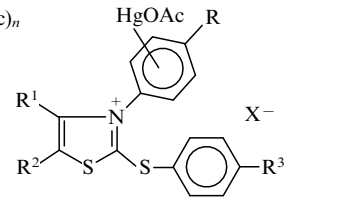


R = Bu, $C_{10}H_{21}$, OBu, OC_8H_{17}; X = OAc, $OCOCF_3$.

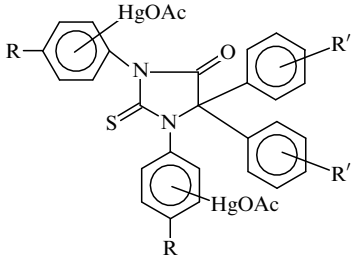
In order to enhance the fungicidal and bactericidal activities of potential pesticides, a series of heterocyclic compounds have been mercurated by mercury acetate in acetic acid.[126 – 130] Mercury then substitutes a hydrogen atom in the benzene ring linked to the nitrogen atom of the heterocycle or to the nitrogen atom of the amino-group in the *para*- (if it is free) or *ortho*-position. Depending on the reactant ratio, mono- and di-mercurated derivatives are formed.



R = H, Br; *n* = 1, 2.[126]

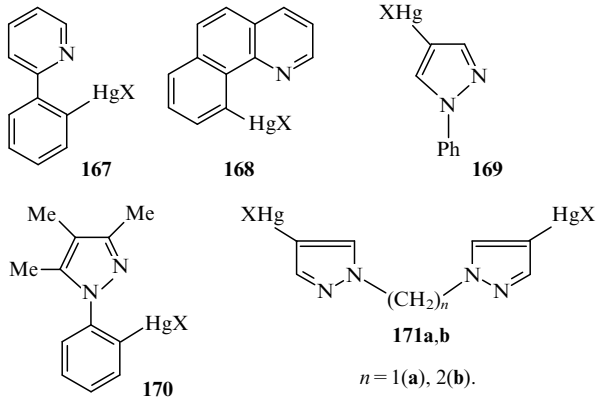


R^1 = Me, R^2 = Et; R^1 = R^2 = Me;
R^3 = H, Hal, Me, OMe, NO_2, COOH.[127]



R, R′ = H, Alk, Hal, NO_2, COOH, OH, $C_{10}H_7$.[128 – 130]

The mercuration of 2-phenylpyridine, benzo[*h*]quinoline, 1-phenylpyrazole, 3,4,5-trimethyl-1-phenylpyrazole, bis(pyrazol-1-yl)methane, and 1,2-[bis(pyrazol-1-yl)]ethane by mercury acetate in alcohol afforded the corresponding OMC **167**–**171a**,**b** in 50%–90% yield.[131,132]



167 **168** **169** **170** **171a**,**b**

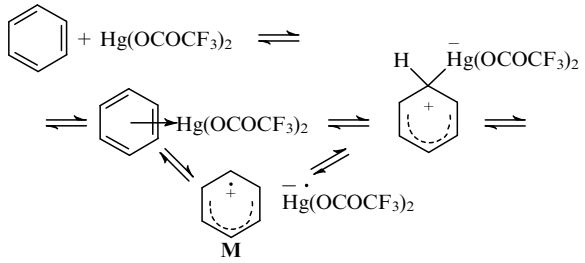
$n = 1$(**a**), 2(**b**).

X = OAc, Cl.

It is difficult to deduce any kind of rules from the above data.[131,132] However, we may note that, as in previous studies,[126–130] in the presence of aryl and heteroaryl fragments in the molecule, mercuration takes place in the benzene ring (regardless of the nature of the substituent in the latter) and does not involve the heterocyclic ring. Only in the absence of an activated benzene ring in the structure of the mercurated compound does mercuration take place in the heterocycle (with formation of compounds **169** and **171a**,**b**). We may note that, as for the majority of pyrazoles entering into S_E reactions, the mode of substitution is determined predominantly by the pyridine nitrogen atom (this can be seen from the study of the mercuration products).

Comparison of the data in Refs 126–130 and in Refs 131 and 132 shows that in the case of compounds **167**, **168**, and **170** the formation of *para*-isomers is not observed at all, whereas Mahapatra and coworkers [126–130] noted their predominant formation.

A special study by the EPR method demonstrated that, in the interaction of mercury trifluoroacetate with certain arenes (acenaphthene, anthracene, biphenyl, *p*-terphenyl, pyracene, hexahydropyracene, and triptycene) in trifluoroacetic acid, type **M** radical-ions are formed initially, which is followed by the effective mercuration of the arenes listed above. The following mechanism of the mercuration of benzenoid aromatic systems with the aid of mercury trifluoroacetate, which includes the generally known [3,7] stages involving the formation of π- and σ-complexes in the corresponding S_E reactions, has been proposed [133] on this basis.

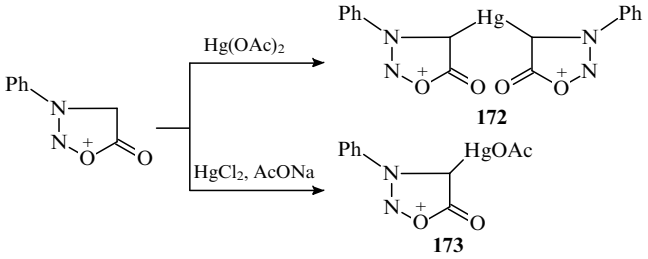


M

$\rightleftharpoons$ $PhHgOCOCF_3 + CF_3COOH$.

Thus the data presented above have shown that aromatic electrophilic mercuration reactions can have, in principle, an oxidation-reduction stage. However, this conclusion is apparently valid only for the most reactive aromatic hydrocarbons [133] and electrophiles with sufficiently marked oxidising properties.

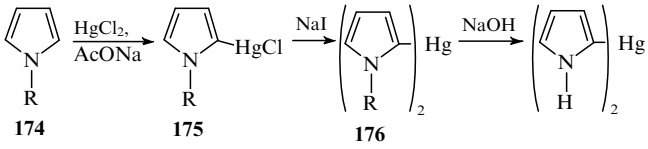
Heterocyclic compounds containing π-electron-excess systems are also readily mercurated by mercury salts.[3] In particular, 3-phenylsydnone is mercurated by mercury(II) chloride or acetate in methanol.[134] Depending on the reaction conditions and the reactant ratio, the fully substituted OMC **172** or 4-acetoxymercurio-3-phenylsydnones **173** are formed.



172 **173**

The sydnone **173** exhibits a high antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*.[134]

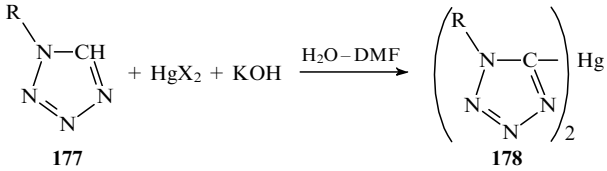
Under analogous conditions, the *N*-substituted pyrroles **174** are mercurated in the 2-position.[135] The OMC **175** obtained are readily symmetrised on treatment with NaI in acetone with formation of the OMC **176**, which afford bis(pyrrol-2-yl)-mercury on interaction with alkali.



174 **175** **176**

R = Ac, O_2SPh.

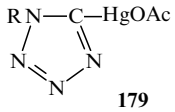
The 1-substituted tetrazoles **177** are smoothly mercurated at room temperature by mercury salts in an alkaline medium at a ring carbon atom with formation of the symmetric *C*-mercuriotetrazoles **178** regardless of the reactant ratio.[136]



177 **178**

R = Me, Ph; X = Br, I, AcO.

In neutral and acid media, the mercuration of the tetrazoles **177** takes place under more severe conditions with formation of either compounds **178** or the 5-acetoxymercurio-derivatives **179** depending on the reactant ratio.[136]



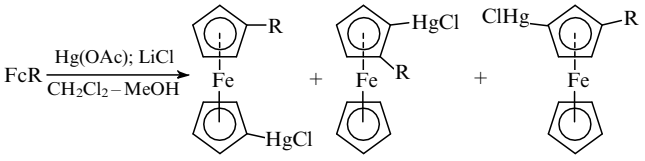
179

It is of interest that 2-substituted tetrazoles do not enter into similar reactions under the conditions described.[136]

Being largely electron-deficient, six-membered π-electron heterocyclic compounds are mercurated with difficulty under severe conditions. Thus the C-mercuration of 2,4-dimethoxypyrimidine by mercury acetate on refluxing in acetic acid with formation of 5-acetoxymercurio-2,4-dimethoxypyrimidine has been described.[137] Various methods for the direct *C*-mercuration of pyrimidine derivatives (uracil, 2-thiouracil, *S*-ethyl-2-thiouracil) as well as purine derivative (theobromine) have been investigated.[138] The following reagents were employed: $HgSO_4 + H_2SO_4$, $Hg(OAc)_2$, $MgO + CF_3COOH$, $Hg(OAc)_2 + HClO_4$, and $Hg(OCOCF_3)_2$. It was found that only uracil is effectively mercurated, affording 5-chloromercuriouracil in 85% yield after the treatment of the reaction mixture with KCl. In other cases, the mercuration of pyrimidine derivatives results in the formation of a mixture of the *C*(5)- and *N*-mercurated compounds in low yields.[138] The mercury-containing heterocycles have been used [138] for the synthesis of the corresponding iodo-derivative by their treatment with a boiling aqueous KI_3 solution.

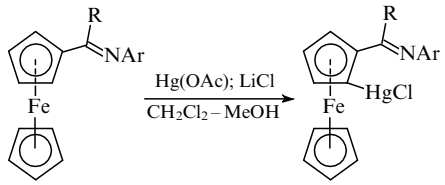
The effect of the mercurating system — a 1 : 1 mixture of mercury acetate with CF_3COOH — on ferrocene has been investigated.[139] It was established that, for the 1 : 1 : 1 ratios of the above reactants in an ether – alcohol mixture at room temperature, ferrocene is smoothly mercurated, giving rise to only the monomercurated product — ferrocenylmercury acetate (yield 86%). Under analogous conditions [139] but with the 2 : 2 : 1 reactant ratios, only the dimercurated product — 1,1′-diacetoxymercurioferrocene — is formed in 67% yield. These compounds are of considerable preparative interest for the synthesis of ferrocene derivatives.

The mercuration of arylferrocenes by treatment with $Hg(OAc)_2$ in a CH_2Cl_2 – MeOH mixture and subsequent treatment of the reaction mixture with an aqueous solution of LiCl led to a mixture of three isomeric OMC, which were separated chromatographically.[140]



R = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$.

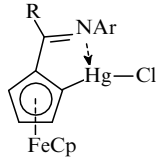
The mercuration of azomethines of the ferrocene series by mercury acetate has been described.[141–146] After the addition of LiCl to the reaction mixture, the corresponding 2-chloromercurio-derivatives were isolated in 60% – 85% yields in all cases.



R = H, Me, Ph; Ar = 4-$MeOC_6H_4$, 4-MeC_6H_4, Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-IC_6H_4, 4-$NO_2C_6H_4$, 3-ClC_6H_4, 3-BrC_6H_4, 3-$NO_2C_6H_4$, α-$C_{10}H_7$, β-$C_{10}H_7$, 2-ClC_6H_4.

The structures of the substances synthesised were investigated by ^1H and ^{13}C NMR and X-ray diffraction methods.[141, 144–146] In particular, the study of the ^{13}C NMR spectra for three series of 2-chloromercurioferrocenylimines (R = H, Me, Ph) led to the discovery of a satisfactory linear correlation between the chemical shifts of the carbon atoms in the ferrocenyl fragment and the Hammett constants σ_m and σ_p of the substituents in the arene ring.[145]

An intramolecular coordinate bond between the Hg and N atoms (2.087 Å) has been discovered in a series of 2-chloromercurioferrocenylimines on the basis of X-ray diffraction data for the latter. It proved to be shorter by 0.35 – 0.45 Å than the sum of the van der Waals radii of the nitrogen and mercury atoms.[141, 144, 146]



R = H, Me, Ph; Ar = Ph, 4-ClC_6H_4.

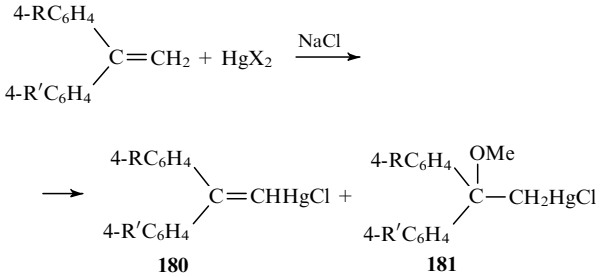
Pentakis(acetoxymercurio)pentamethylruthenocene has been obtained in 88% yield by the reaction of pentamethylruthenocene with mercury acetate (molar ratio 1 : 5) in the 1 : 1 ethanol – ether mixture.[147] It is halogenated on treatment with KI_3 or KBr_3 with formation of the corresponding pentahalopentamethylruthenocenes. The structures of the compounds have been established by X-ray diffraction.

The direct mercuration of *o*- and *m*-carbaboranes by treatment with HgO in CF_3COOH has been achieved.[148] It leads to the substitution of the hydrogen atom at the boron atom in the 9-position in the carbaborane ring by mercury. The mercuration of the dicarbaboranyl Fe(III),[149] Ni(IV), and Co(III) [150] complexes takes place in the same position and under the same conditions.

$$(C_2B_9H_{11})_2M \xrightarrow[NaCl]{HgO + CF_3COOH} (C_2B_9H_{10}HgCl)_2M$$

M = Fe, Ni, Co.

1,1-Diarylethenes have an excess π-electron density, as a result of which it is possible to achieve their electrophilic vinylmercuration on treatment with an equimolar amount of HgX_2 in acetonitrile or an ether – THF mixture with formation of compounds **180**.[151]



180 **181**

R = R′ = H, Me, Cl, MeO; R = F, R′ = MeO;

R = Cl, R′ = Me; X = BF_4, CF_3COO.

If the reaction is carried out in methanol, then electrophilic substitution and conjugate addition of the mercury salt to the double bond result in the formation of a mixture of the products **180** and **181**, the ratio of which depends on the initial reactant ratio.[151]

VII. Mercuration of CH acids

Apart from aromatic compounds, compounds with mobile hydrogen atoms, capable of giving rise to a stable carbanion, may be mercurated.[152] The range of such compounds proved to be fairly wide.[4–7] and it has been increasing continuously in connection with the synthesis of new substances and with the search for new mercurating agents. In particular, the reactions involving the α-mercuration of a large series of CH acids having $pK_a < 29$ with the aid of $Hg[N(SiMe_3)_2]_2$, have been investigated [153, 154] which led to the synthesis of the symmetrical fully substituted OMC **182** in 50% – 85% yield.[3] Heating of compounds **182** with $HgCl_2$ in water or ethanol affords the corresponding chloromercurio-derivatives **183**.[153]

$$RH + [(Me_3Si)_2N]_2Hg \longrightarrow \underset{\mathbf{182}}{RHgR} \xrightarrow{HgCl_2} \underset{\mathbf{183}}{RHgCl}$$

R = , $AcCH_2$, $(PhCO)_2CH$, NC(Ph)CH, PhC≡C,

$Ac_2(Me)C$, $Ac_2(Et)C$, $Ac_2(Ph)C$.

Weaker CH acids — acetonitrile and pinacolin ($pK_a > 31$) — could not be made to undergo this reaction.[153]

It has been observed recently [94] that MDNA readily mercurates compounds with mobile hydrogen atoms such as acetone, acetylacetone, and malonic, nitroacetic, and nitromalonic esters in nonpolar and polar organic solvents, as well as water. The mercuration of acetone and acetylacetone by MDNA at room temperature in ether leads to the substitution of only one hydrogen atom, whilst the mercuration of the nitroacetic and malonic esters under the same conditions affords dimercurated products.[94]

$$AcOCH_2R + Hg[N(NO_2)_2]_2 \xrightarrow[\mathbf{121}]{} \longrightarrow MeCOCHRHgN(NO_2)_2 + HN(NO_2)_2$$

R = H, Ac.

$$RCH_2COOR' + \mathbf{121} \longrightarrow R\overset{\displaystyle HgN(NO_2)_2}{\underset{\displaystyle HgN(NO_2)_2}{C}}COOR' + 2HN(NO_2)_2$$

R = NO_2, R′ = Me; R = COOEt, R′ = Et.

The reaction of malonic ester with MDNA in water [94] leads only to oligomeric products, the elemental analysis of which yields a result approximately to corresponding to the formula

$(NO_2)_2NHgC(COOEt)_2HgC(COOEt)_2HgC(COOEt)_2HgN(NO_2)_2$.

Heating of MDNA with malonic ester without a solvent for 30 min at 100 °C gives rise to a sparingly soluble product which does not contain the $N(NO_2)_2$ group at all and, according to the authors,[94] is a polymer $[-CR_2Hg-CR_2Hg-]_n$. The mercuration of dimethyl nitromalonate with MDNA results in the immediate formation of a fully substituted symmetrical OMC.[94]

$$O_2NCH(COOMe)_2 + \mathbf{121} \xrightarrow{H_2O} Hg[C(NO_2)(COOMe)_2]_2.$$

The *C*-mercuration of bis(diphenylphosphino)methane **184** with a mixture of $Hg(AcO)_2$ and $Hg(CF_3SO_3)_2$ in methanol using reactant ratios of 1 : 2 : 1 and 1 : 3 : 1 has been achieved.[155] This resulted in the quantitative synthesis of the di- and tri-mercurated compounds **185** and **186**, the structures of which have been confirmed by ^{31}P and ^{199}Hg NMR spectroscopic data.

$$CH_2(PPh)_2 \;\mathbf{184}\;\begin{cases}\xrightarrow[(CF_3SO_3)_2Hg]{2Hg(OAc)_2} [AcOHgCH(\overset{+}{P}Ph_2HgOAc)_2](CF_3SO_3^-)_2 \;\mathbf{185}\\ \xrightarrow[(CF_3SO_3)_2Hg]{3Hg(OAc)_2} [(AcOHg)_2C(\overset{+}{P}Ph_2HgOAc)_2](CF_3SO_3^-)_2 \;\mathbf{186}\end{cases}$$

The mercuration of certain aliphatic carboxylic acids **187** has been investigated.[156–158] The direct mercuration of compound **187** on heating (120 °C, 5–6 h) with $Hg(OCOCH_2R)_2$ afforded the oligomers **188** with traces of the product **189**.

$$RCH_2COOH\;\mathbf{187}\xrightarrow{Hg(OCOCH_2R)_2}\longrightarrow RCH_2CO\left[-Hg-\underset{R}{CH}-CO-\right]_nH \;\mathbf{188} + RCH_2CO\left[-Hg-\underset{HgCOCH_2R}{\overset{R}{C}}-CO-\right]_nH \;\mathbf{189}$$

R = H, Me, Et, Pr, Pr^i; n = 4–10.

The interaction of the oligomers **188** and **189** with 0.1 M HCl or HNO_3 solution leads to the formation of the monomeric OMC **190** and **191** in high yields (50%–76%).

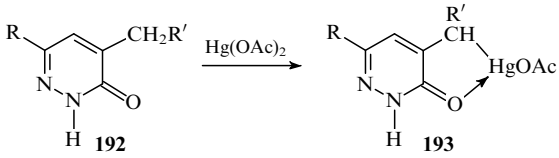
$$\mathbf{188, 189}\xrightarrow{HX}\begin{cases}\rightarrow RCH(HgX)COOH\;\mathbf{190}\\ \rightarrow RC(HgX)_2COOH\;\mathbf{191}\end{cases}$$

X = Cl, NO_3.

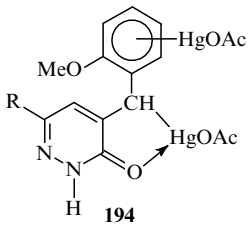
Thus the set of the reactions described above may be regarded as a convenient method for the α-mercuration of the simplest aliphatic carboxilic acids.

The reactions involving the CH acid groups of a series of heterocyclic compounds are extremely interesting. Thus the interaction of 3-R-5-(R′CH_2)-pyridazin-1*H*-6-ones **192** with mercury acetate on refluxing the reagents in acetic acid leads to the *C*-α-mercuration at the CH_2 group [159] by virtue of the electron-accepting influence of the pyridazine ring, which increases the mobility of the hydrogen atoms in the α-position of the substituent.

If the benzene ring in the molecule of compound **192** is activated by electron-donating substituents, it too is mercurated.[159] Thus, together with the product **193** of the mercuration of the CH acid group, the dimercuration product **194** is formed on mercuration of the pyridazine **192** (R′ = 2-$MeOC_6H_4$).

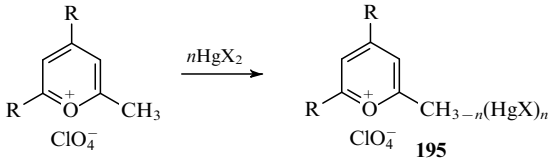


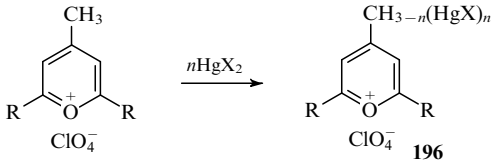
R = R′ = Ph, 4-MeC_6H_4, 2-$MeOC_6H_4$; R′ = H, Me.



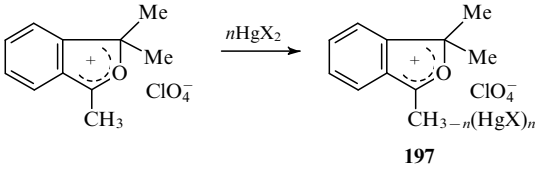
The structures of compounds **193** and **194** have been established on the basis of ^1H NMR, UV, and IR spectroscopic data.[159]

The mercuration of α- and γ-methylpyrylium perchlorates [160] and also of a 1-methylphthalylium salt [161] leads to the corresponding mercury-containing methylpyrylium and phthalylium perchlorates **195**–**197**. The reactions proceed readily on brief refluxing of the salts of the heterocyclic cations and HgX_2 in ethanol [160] or glacial acetic acid.[161] Depending on the reactant ratio, the mono-, di-, and tri-mercurated compounds **195**–**197** are then formed in 60%–100% yields.





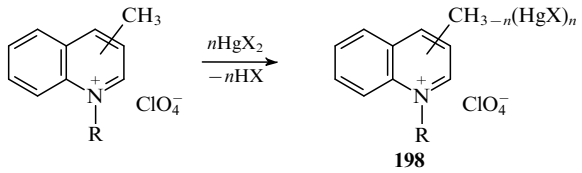
R = Ph, 4-$EtOC_6H_4$, Me; n = 1–3, X = OAc, $OCOCF_3$.



X = OAc, $OCOCF_3$; n = 1, 2.

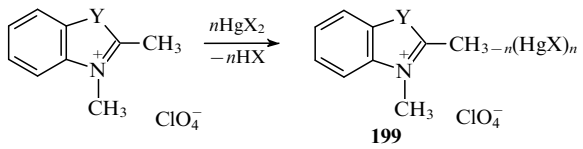
It is of interest to note that in the case of the 1,3,3-trimethylphthalylium cation only the methyl group in the 1-position is mercurated. The methyl groups in the 3-position are not mercurated even when an excess of the mercurating agent is employed, which can probably be explained by the lower mobility of the hydrogen atoms in these groups.

The mercuration of 2- and 4-methylquinolinium,[162] 1,2-dimethylbenzoxazclium, 1,2-dimethylbenzothiazolium, 1,2,3-trimethylbenzimidazolium,[163] and 1,2-dimethyl-4,6-diphenylpyridinium [164] salts with mercury acetate or trifluoroacetate, leading to the formation of compounds **198**–**200** respectively, has been achieved under similar conditions.



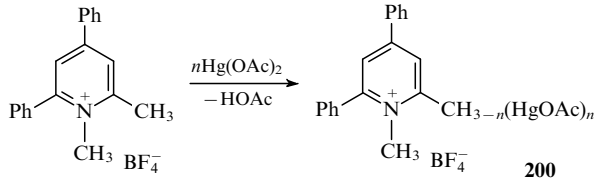
198

R = Et, Ph; X = OAc, $OCOCF_3$; $n = 1-3$.



199

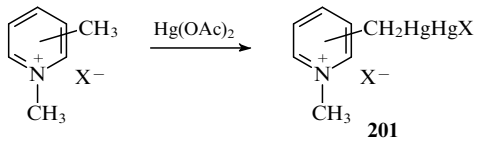
Y = O, S, NMe; X = OAc, $OCOCF_3$; $n = 1-3$.



200

$n = 1-3$.

However, the mercuration of 1,2- and 1,4-dimethylpyridinium salts under the same conditions yielded [164] the salts **201** with a Hg–Hg bond, which are stable at room temperature.



201

X = I, ClO_4, OAc.

We may note that in all the heterocyclic systems enumerated, only the methyl group in the α- or γ-position relative to the heteroatom is mercurated. The mercuration of the alkyl group (Me, Et) linked directly to the ring nitrogen atom has never been observed.

The structures of the salts **195**–**201** have been established [160–164] by studying their chemical properties and on the basis of the results of elemental analysis, as well as ^{1}H NMR and IR spectroscopic data. The salts are of preparative interest for the synthesis of functionally substituted salts of heterocyclic cations, because the mercury-containing groups may be comparatively readily substituted by other groups.[3]

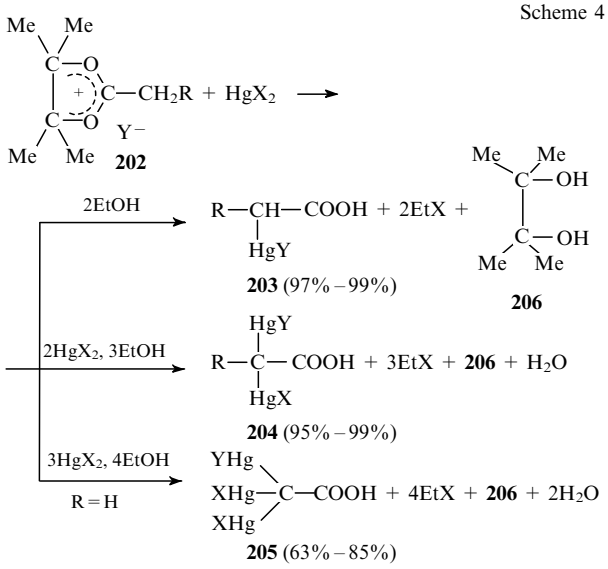
Furthermore, studies on the antimicrobial activities of the α-alkylmercurated pyrylium salts **195** and **196**, the pyridinium salts **200** and **201**, the quinolinium salts **198**, and the benzazolium salts **199** have shown [165] that this group of mercury-containing heterocyclic compounds possesses a striking antimicrobial activity with a wider activity spectrum than the familiar preparations.

Somewhat unusual results have been obtained [166] on mercuration of 2-alkyl-substituted 4,4,5,5-tetramethyl-1,3-dioxolanium salts **202** with mercury acetate or trifluoroacetate. In this case, the 1,3-dioxolane ring is opened in the course of mercuration on refluxing the reactants, which results in a high yield of α-mercurio-substituted carboxylic acids **203**–**205**, the ethyl esters of acetic or trifluoroacetic acid, and pinacol **206**. Depending on the molar reactant ratio, monomercurated (compound **203**), dimercurated (compound **204**), and trimercurated (compound **205**) carboxylic acids are obtained. According to elemental analysis and IR spectra,[166] the YHg group always enters into their compositions regardless of the nature of the mercurating agent (Scheme 4).

Thus the reactions constitute a convenient method of synthesis of α-mercurated carboxylic acids.

Successive treatment of the η^6-fluorene-η^5-cyclopentadienyliron cation with Bu^{t}OK and HgX_2 mercury salts in a 1:1 MeCN–dimethylcellosolve mixture led to the synthesis [167] of the corresponding mercury-containing complexes **207** for the first time. Mono- and di-mercurated compounds **207** are formed in 75%–82% yield depending on the molar reactant ratio.[167]

Scheme 4



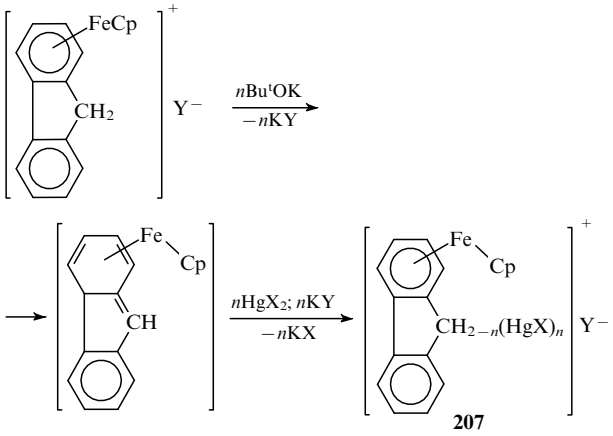
202

203 (97%–99%) **206**

204 (95%–99%)

205 (63%–85%)

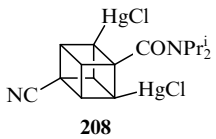
R = H, Me; Y = ClO_4, BF_4; X = OAc, $OCOCF_3$.



207

X = OAc, $OCOCF_3$, Cl; Y = BF_4, PF_6; $n = 1, 2$; Cp = C_5H_5.

An interesting method for the mercuration of cubanes has been described for 4-cyano-1,1-diisopropylcarbamoylcubane as an example.[168] Successive treatment of the cubane with the lithium–tetramethylpiperidine–$MgBr_2$ system and then with $HgCl_2$ leads to the dimercurated cubane **208**.



208

VIII. Mercuration by organomercury salts and hydroxides

The reactions presented in this section can be regarded as a direct method for the synthesis of asymmetric fully substituted OMC containing different types of Hg–element bonds.

The interaction of the organomercury hydroxides RgOH **209** (R = Ph, CH_2Ph, cyclo-C_6XH_{11}) with the nitriles PhCH(R′)CN (R′ = H, Et, Ph) has been investigated.[169]

Depending on the nature of the group R in the molecule of the hydroxide **209** and the reaction conditions, mixtures of monomercurated (compound **210**) and dimercurated (compound **211**)

derivatives or only the dimercurated compounds are formed from phenylacetonitrile.[169] In the presence of small amounts (5% – 10%) of KOH, only the dimercurated compounds **211** are obtained.

$$\underset{\mathbf{209}}{PhCH_2CN + RHgOH} \xrightarrow{EtOH} \underset{\mathbf{210}}{PhCH(HgR)CN} + \underset{\mathbf{211}}{PhCCN(HgR)_2}$$

R = Ph, CH_2Ph.

Cyclohexylmercury hydroxide does not react with $PhCH_2CN$ even in the presence of KOH. When Ph_2CHCN interacts with compound **209**, metallic mercury is liberated and the dimer **212** is formed, while PhCH(Et)CN does not react with compound **209** at all.[169]

$$2Ph_2CHCN + \mathbf{209} \xrightarrow{EtOH} \underset{\mathbf{212}}{Ph_2C(CN)-C(CN)Ph_2} + Hg + RH + H_2O.$$

According to ^{199}Hg NMR data, compound **210** (R = Ph) is partly symmetrised in solutions in chloroform and pyridine.[169]

$$\underset{\mathbf{210}}{2PhCH(HgPh)CN} \rightleftharpoons Ph_2Hg + \left[PhCH(CN)-Hg\right]_2$$

However, in the solid state it is an individual compound. This is indicated indirectly by the depression of the melting point (by 20 – 25 °C) of the prepared mixture of compound **210** and $HgPh_2$. IR and NMR spectroscopic data have shown that compounds **210** and **211** exist mainly as the C-form.[169]

Treatment of malonodinitrile with RHgX leads to the formation of only the dimercurated product.[170]

$$CH_2(CN)_2 + 2RHgX \longrightarrow (RHg)_2C(CN)_2$$

R = Ph, CH_2Ph; X = OH, OAc.

The organomercury derivatives **213**, which exists mainly in the C-form, have been obtained by treating the substituted dinitriles $RCH(CN)_2$ with organomercury hydroxides R′HgOH or acetates R′HgOAc.[171]

$$RCH(CN)_2 + R'HgOH \xrightarrow[-H_2O]{EtOH} \underset{\mathbf{213}\ (60\%-80\%)}{R-C(CN)(HgR')-CN}$$

R = Me, Ph; R′ = Ph, CH_2Ph.

It is of interest to note that a degenerate exchange reaction, occurring with dissociation of the C – Hg bond, has been observed[171] for the phenylmercury derivative of methylmalonodinitrile.[171] Nevertheless, the organomercury dinitriles **213** are not symmetrised in solution,[171] in contrast to the organomercury derivative of phenylacetonitrile **210** investigated earlier.[169]

The organomercury salt $CF_3HgOCOCF_3$ interacts readily[88] with unsaturated compounds capable of being deprotonated in an alkaline medium.

$$RH + CF_3HgOCOCF_3 \xrightarrow{NaOH} RHgCF_3 + NaOOCCF_3$$

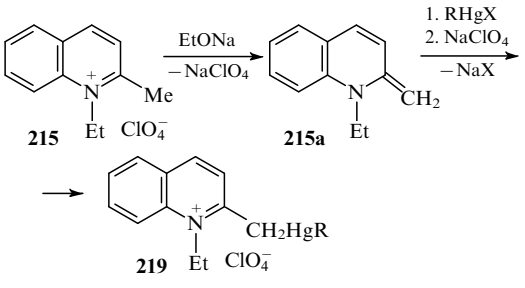
R = PhC≡C, $Cl_2C{=}CCl$.

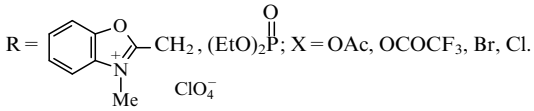
The reaction of RHgOMe with hydrogen peroxide in methanol afforded the OMC **214**.[172]

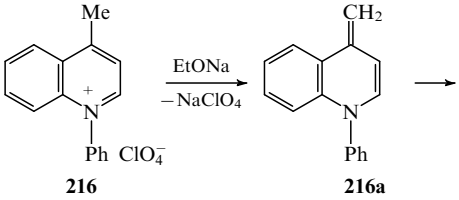
$$2RHgOMe + H_2O_2 \longrightarrow \underset{\mathbf{214}}{RHgOOHgR} + 2MeOH$$

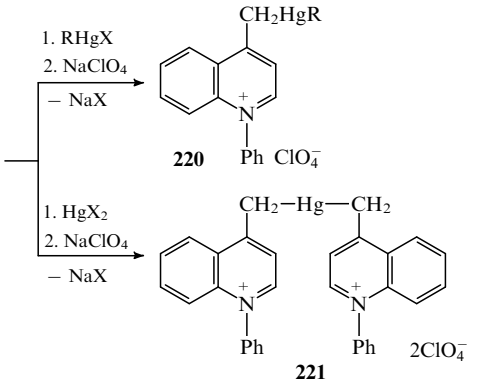
In benzene, diethyl ether, and methylene chloride, compounds **214** interact with an excess of H_2O_2 and are converted into the hydroperoxides RHgOOH. However, according to IR spectroscopic data,[172] the latter are complexes of the type $(RHgO)_2 \cdot H_2O_2$

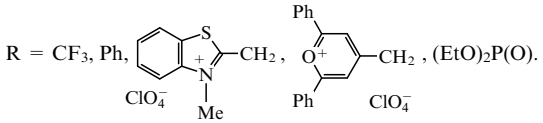
A new method of synthesis of fully substituted mercury-containing salts of heterocyclic cations has been described.[173] Successive treatment of 2- and 4-methylquinolinium (compounds **215** and **216**), 4-methyl-2,6-diphenylpyrylium (compound **217**), and 1,2-dimethylbenzothiazolium (compound **218**) perchlorates with an equimolar amount of a base (EtONa, Bu^tOK, NEt_3) and then with an equimolar amount of organomercury salts RHgX led to the synthesis[173] of the fully substituted 4-methylenemercury-containing salts of the corresponding heterocyclic cations **219** – **224** in 61% – 83% yield.

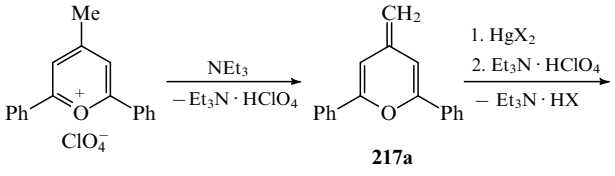


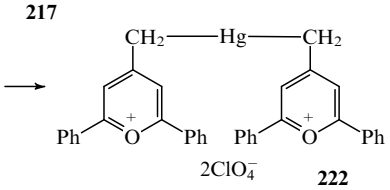


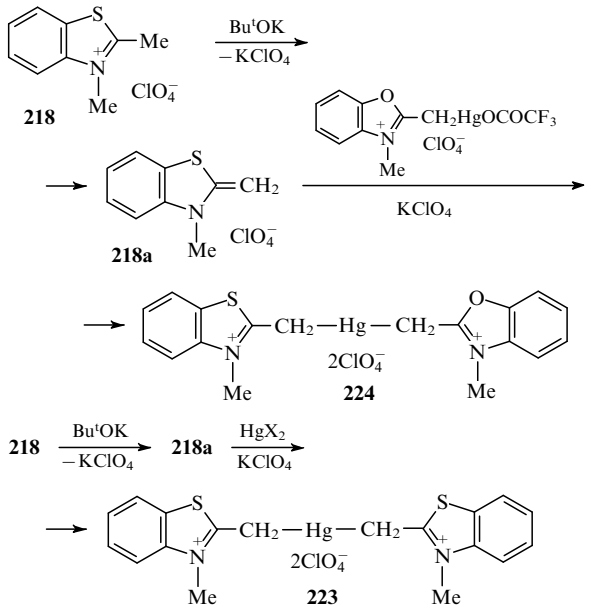








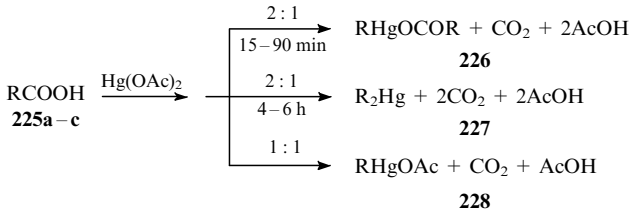




Thus the reactions involving the mercuration of the methylene derivatives of the heterocyclic bases **215a–218a** by mercury salts or organomercury reagents presented above make it possible to obtain diverse symmetrical (compounds **221–223**) and asymmetric (compounds **219**, **220**, and **224**) fully substituted 2- and 4-methylenemercurated salts of heterocyclic cations. The method is simple to use and is extremely general, and is therefore promising for the synthesis of new OMC.

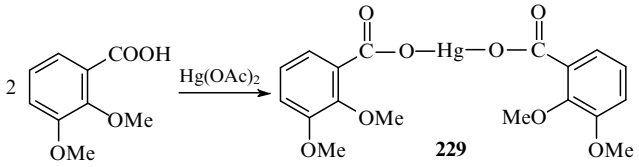
IX. Other methods of synthesis of organomercury compounds

The interaction of polymethoxybenzoic acids **225** with mercury acetate in proportions of 2:1 proceeds in an unusual manner, leading even under mild conditions (aqueous methanol, 20 °C, 15–90 min) to different decarboxylation products **226–228** depending on the molar reactant ratio and the reaction time.[174]

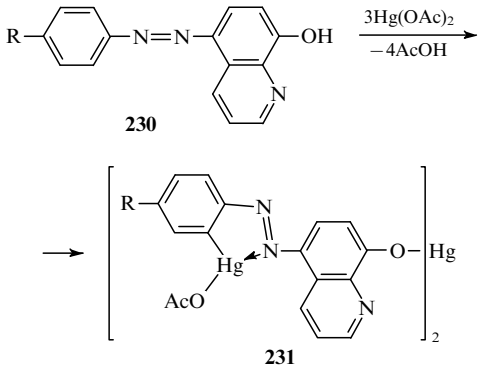


R = 2,6-$(MeO)_2C_6H_3$ (**a**); 2,3,4-$(MeO)_3C_6H_2$ (**b**); 2,4,6-$(MeO)_3C_6H_2$ (**c**).

The reaction of $Hg(OAc)_2$ with 2,3-dimethoxybenzoic acid leads to the mercury salt **229**, while in the case of 3,4,5-trimethoxybenzoic acid the reaction does not proceed at all.[174]



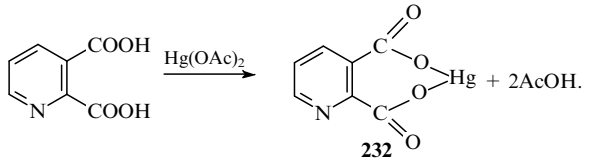
The azo-coupling reaction of compound **230** with $Hg(OAc)_2$ proceeds with formation of the products of dimercuration at the carbon and oxygen atoms (compound **231**).[175]



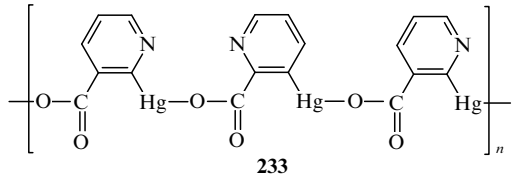
R = H, Me, NO_2.

On the other hand, treatment of compound **230** with $HgCl_2$ results in the formation of only a 1:1 complex, the structure of which has not been established.[175]

The interaction of quinolinic acid with mercury acetate in aqueous acetic acid leads to the formation of mercury pyridine-2,3-dicarboxylate **232**.[176]



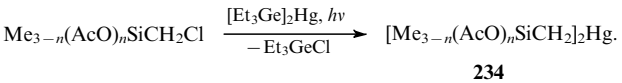
A 9:1 mixture of 2-carboxylatopyridin-3-ylmercury and 3-carboxylatopyridin-2-ylmercury, which according to the authors have a polymeric structure of type **233** with a C–Hg–O linkage, has been obtained by the decarboxylation of the **232** in DMSO at 190 °C for 1 h.



$n = 2–3$.

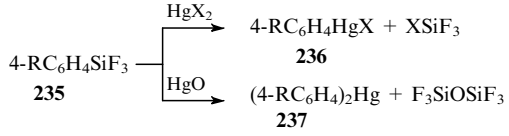
The structures of compounds **232** and **233** have been confirmed by IR and ^1H, ^{13}C, and ^{199}Hg NMR spectroscopic data as well as mass-spectrometric data.[176]

A method has been developed [177] for the synthesis of bis(acetoxysilylmethyl)mercury compounds **234** in 80%–90% yields. It is based on the photoinitiation reaction of bis(triethylgermyl)mercury with acetoxychloromethylsilanes.



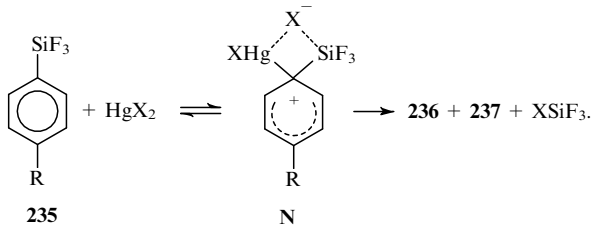
The structure of the mercury compounds **234** has been confirmed by NMR spectroscopic data. It has been noted that ^2J(Hg–Si), ^2J(Hg–H), and ^2J(Hg–C) increase with increase in the number of acetoxy-groups bound to the silicon atom.[177]

When the Si–C bond in aryltrifluorosilanes **235** dissociated on treatment with mercury salts HgX_2 or HgO, asymmetric (compound **236**) and symmetrical (compound **237**) OMC are formed in high yields.[178]



R = H, Me, Cl, Br, NO_2; X = Cl, Br, I, CN, OAc.

It has been noted that electron-donating substituents facilitate the above reactions,whilst electron-accepting ones hinder them. This permits certain conclusions about the reaction mechanism, which can be represented by the following scheme in a general form:[8]



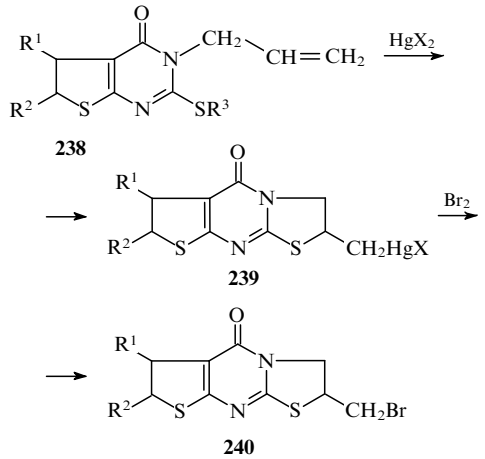
There is no doubt that the more effective stabilisation of the cyclic transition state **N** as a result of the delocalisation of the positive charge is attained in the case of electron-donating substituents R, which thus promote the formation of the corresponding reaction products **236** and **237**.

Mercury salts HgX and HgO also cleave the Si–C bond in chloromethyltrifluorosilanes $F_3SiCH_{3-n}Cl_n$ ($n = 1-3$) with formation of the corresponding derivatives $XHgCH_{3-n}Cl_n$ or $Hg(CH_{3-n}Cl_n)_2$ in 18%–30% yields.[178] The replacement of a fluorine atom in organyltrifluorosilanes by an alkyl group hinders the cleavage of the Si–C bond.

A method of synthesis of dimethylmercury by the interaction of methylhydrazine with mercury oxide in diethylether has been described.[179]

$$2MeNHNH_2 + HgO \longrightarrow \underset{(10\%)}{Me_2Hg} + N_2 + H_2O.$$

The interaction of mercury salts with derivatives of thieno-[2,3-*d*]pyrimidines **238** has been achieved.[180] It was shown that the solvatomercuration of compound **238** in ethanol or methanol is accompanied by their intramolecular cyclisation with participation of the sulfur atom of the thioureide group, which leads to the formation of the tricyclic system **239** with a mercury-containing substituent.



$R^1 = R^2 = Me$; $R^1 + R^2 = (CH_2)_3$, $(CH_2)_4$; $R^3 = H$, COPh; X = Cl, Br.

The structure of the tricyclic system **239** has been confirmed by ^1H NMR and IR spectroscopic data and also by the reaction with bromine, which leads to the bromo-derivatives **240** already known.[180]

X. Conclusion

The data examined in the present review show that studies designed to expand the applications of already known methods and to develop new methods of synthesis of organomercury compounds have been prosecuted vigorously in recent years. This has led to the availability of a wide range of organomercury compounds in which mercury is bound to fragments of diverse organic molecules — aliphatic, carbocyclic, aromatic, heterocyclic, organometallic, *etc*. The range of the possible practical ways of using the mercury-containing compounds obtained is extremely wide.[2,7] Thus many of the newly synthesised compounds can be regarded as potential medicinal preparations with antibacterial[113,115] and antimicrobial[126,134,165] properties and also as chemical agents for the protection of plants, acting as nematocides,[128,129,137] fungicides,[128,129] and insectoacaricides.[121]

Thus the search for and development of new methods of synthesis of organomercury compounds have not lost current interest because these compounds have found applications in various branches of science, industry, medicine, and agriculture.

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