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Free Radical Reactions of Organomercurials[†]

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I. Introduction

Organomercury compounds[1-8] have been known since the middle of the past century, and they were one of the first types of organometallic compounds studied. However, due to the low reactivity of the mercury–carbon bond, their application in synthetic organic processes was not important, and their utility was centered on the synthesis of other more reactive organometallics. This low importance was even more diminished when the Grignard reagents were discovered at the beginning of this century. However, in the past 20 years, organomercury compounds have again acquired interest in organic synthesis, in spite of their toxicity, in relation mainly to the solvomercuration reaction, which permits the preparation of functionalized organomercurials with high selectivity; these organometallics are adequate precursors for functionalized organic compounds.

The numerous general methods for obtaining organomercury compounds are described in detail in *Houben-Weyl*[3] and include, basically, substitution or addition reactions; they are shown as follows:

(a) Substitution reactions

$$RH + HgX_2 \rightarrow RHgX + HX$$

(R = alkyl, alkynyl, aryl)

$$RMet + HgX_2 \rightarrow RHgX + MetX$$

$$RMet + RHgX \rightarrow R_2Hg + MetX$$

$$(Met = Li, \tfrac{1}{2}Mg, \tfrac{1}{3}B, \tfrac{1}{3}Al, \tfrac{1}{3}Tl, \tfrac{1}{4}Si, \tfrac{1}{2}Zn, \tfrac{1}{4}Pb, ...)$$

$$RX + Hg \rightarrow RHgX$$

$$(X = Br, I, N_2^+, NHNH_2)$$

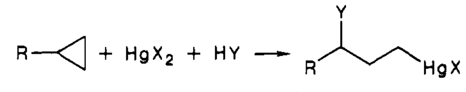
(b) Addition reactions

$$RCH{=}CH_2 + HgX_2 + HY \rightarrow RCHY{-}CH_2HgX$$

$$(Y = OH, O_2H, OR', O_2R', OAc, NR'_2, NHCOR', N_3, NO_2)$$

$$RC{\equiv}CR + HgX_2 \rightarrow RCX{=}CR(HgX)$$

$$(X = F, Cl, OAc, SCN)$$



(Y = OH, OR')

The reactivity[3] of the prepared organomercury compounds can be summarized in the following way:

(a) Mercury–metal interchange (transmetalation)

$$RHgX + Met \rightarrow RMet + Hg + X^-$$

$$R_2Hg + 2Met \rightarrow 2RMet + Hg$$

$$(Met = Li, Na, K, Mg, Al, ...)$$

This reaction is particularly interesting for obtaining β-functionalized organometallic intermediates derived from alkaline-earth metals.[9]

(b) Mercury–hydrogen interchange (hydrogenolysis) by means of mineral acids or reducing agents, especially sodium borohydride

$$RHgX + HX \rightarrow RH + HgX_2$$

$$RHgX + H^- \rightarrow RH + Hg + X^-$$

[†] This review is dedicated to the memory of Professor Vicente Gómez-Aranda.

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José Barluenga was born in Tardienta, Spain, in 1940. He obtained his Ph.D. degree (solvomercuration of dienes) at the University of Zaragoza in 1966 under the direction of Prof. V. Gómez-Aranda. Following this, he spent 3.5 years as a postdoctoral research fellow of the Max Planck Gesellschaft at the Max Planck Institut für Kohlenforschung, Mülheim a.d. Ruhr, Germany, in the group of Prof. H. Hoberg studying aluminum chemistry. In 1970 he took a position as a Research Associate at the University of Zaragoza, where he was promoted to Associate Professor in 1972. In 1975 he moved to the University of Oviedo as Professor in Organic Chemistry, in the Department of Organometallic Chemistry, where he is now head of the group of organic synthesis. His major research interest is focused on the development of new synthetic methods in the area of heterocyclic chemistry and functionalized systems. He has published a number of publications in this area involving mercury salts and also organoalkaline and organomagnesium compounds.

Miguel Yus is currently Professor in Organic Chemistry at the University of Oviedo, Spain. He received his B.S. degree in 1969 and his Ph.D. degree in 1973 from the University of Zaragoza (under the direction of V. Gómez-Aranda and J. Barluenga). After 2 years of postdoctoral study (Max Planck Institut für Kohlenforschung, Mülheim a.d. Ruhr, Germany), he joined the Faculty of Chemistry of the University of Oviedo. He was a visiting scientist at ETH-Zürich, CH (1983), at the University of Oxford, UK (1984), and at Harvard University (1985). His research interests are focused on new methodology in organic synthesis by means of organometallic reagents.

(c) Mercury–carbon interchange in the presence of a catalyst

$$\mathrm{RHgX + CO + R'OH \xrightarrow{Pd^{II}\ cat.} RCO_2R'}$$

$$\mathrm{RHgX + CO \xrightarrow{Ni^{0}\ cat.} RCO_2R'}$$

$$\mathrm{R_2Hg + R'COCl \xrightarrow{AlBr_3} RCOR'}$$

$$\mathrm{RHgX + R'Cl \xrightarrow{Pd^{II}\ cat.} RR'}$$

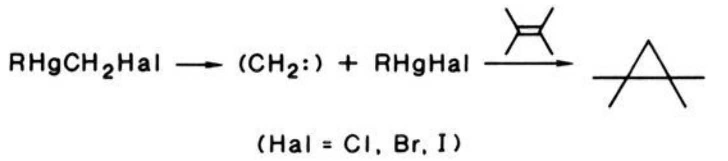
$$\mathrm{RHgX + CH_2{=}CHR' \xrightarrow{Pd^{II}} RCH{=}CHR'}$$

(d) Mercury–halogen interchange (halodemercuration)

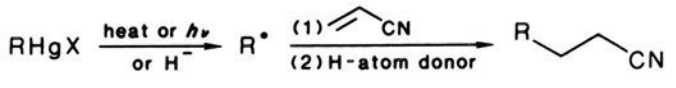
$$\mathrm{RHgX + Hal_2 \rightarrow RHal + XHgHal}$$

$$\mathrm{(Hal = Br, I)}$$

More recently, different methods for the generation of carbenes and radicals from organomercury compounds have been developed. In the first case, the starting materials are haloalkylmercury compounds:[8,10]



In the generation of radicals[11,12] the starting materials are typical organomercury compounds; the thermal, photochemical, or chemical—mainly using a hydride—treatment of these organometallics yields the corresponding radicals:



From the above-described reactivity, it can be deduced that organomercury compounds are adequate precursors for carbanions (transmetalation), carbocations (halodemercuration), carbenes, or radicals. From these possibilities, the transformations of organomercury compounds, which involve intermediate radicals, have acquired great interest in the past decade due to the importance in organic synthesis of radical reactions, which have been developed in the past years, above all in the important field of carbon–carbon bond formation.[11-17]

The present review considers the reactions of organomercury compounds, which occur through a radical mechanism, paying special attention to their potentiality in organic synthesis, that is, pointing out the applicability of these processes.

II. Radicals Generated Thermally or Photochemically

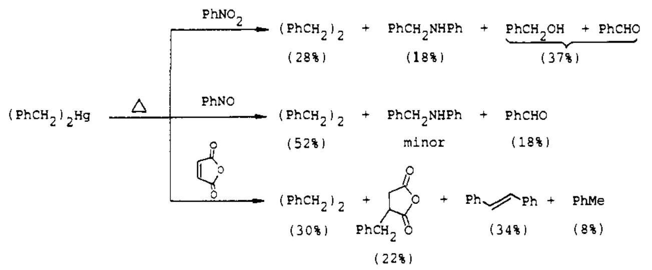
A. General Theoretical Comments

The thermal generation in solution of substituted benzyl radicals from substituted dibenzylmercury[18-23] or benzylmercury iodides[24] has extensively been studied from a theoretical and spectroscopic point of view. Thus, the kinetics of the decomposition of these mercurials has been investigated, concluding that they are processes of first order,[18-21] the corresponding values of σ have been deduced (although these might be flawed because benzyl mercurials decompose by a chain mechanism),[22] and the resulting radicals have been studied by spin resonance spectroscopy (ESR).[25] This theoretical and spectroscopic study has been extended to diarylmercury[24] or dialkylmercury compounds,[26] fluoroalkylmercury derivatives,[27] and β-substituted organomercurials.[28]

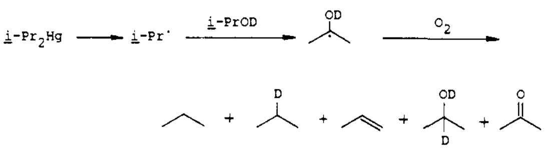
B. Thermally Generated Radicals

The most studied generation of radicals by heating[29] has been carried out starting from dibenzylmercury.

SCHEME 1[31-33]



SCHEME 2[45]



The reaction has no synthetic utility because a mixture of reaction products is usually obtained, 1,2-diphenylethane always being present. Thus, while dibenzylmercury reacts with acetic acid at 130 °C, yielding benzylmercury benzoate as the main product,[30] its treatment with nitrobenzene[31] or nitrosobenzene[32] leads to a mixture of different compounds (Scheme 1). When decomposition is performedin the presence of maleic anhydride, the mixture indicated in the Scheme 1 is obtained.[33] The corresponding radical produced by reaction of the benzyl radical with the anhydride is postulated as an intermediate.

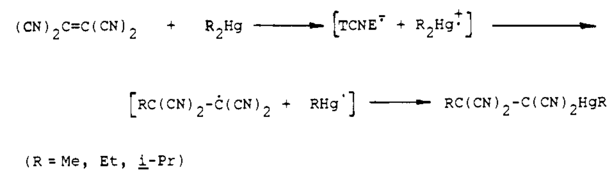
Perhaps the most studied reaction with the benzyl radical thermally generated from dibenzylmercury is the process with aromatic systems such as anthracene,[34-36] 9,10-dihydroanthracene,[36-38] pyridine,[39] quinoline,[39] isoquinoline,[39] and indene.[40] In all these cases the reaction is initiated by generation of the benzyl radical, which attacks the aromatic system, yielding a new radical; the final stabilization of this intermediate leads to the corresponding mixture of products. An indirect route for generating benzyl radicals is to thermally decompose dimethyl-[41] or diethylmercury[42] in the presence of toluene.

The pyrolytic decomposition of diphenylmercury[36,40,43] or phenylmercury acetate[44] as a source of phenyl radicals and their coupling reaction with aromatic systems such as anthracene,[43] 9,10-dihydroanthracene,[36] or indene[40] have also been described.

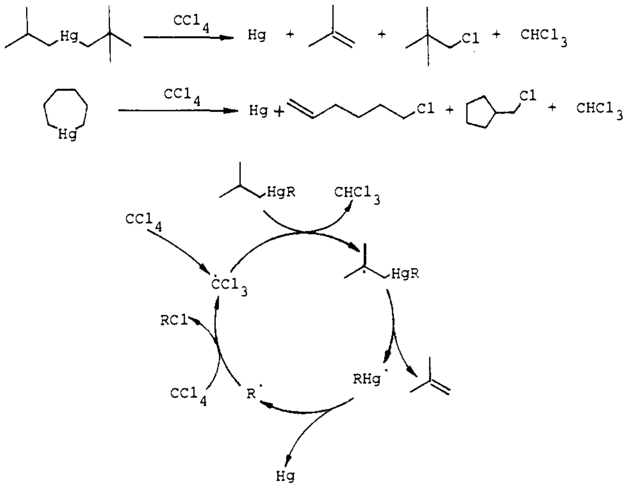
The pyrolysis of different dialkylmercury compounds in the presence of 2-propanol leads to the radical derived from the alcohol, which suffers disproportionation or oxidation, giving, in the case of diisopropylmercury, the products showed in Scheme 2. The process, which can also be activated photochemically, has been studied by using *O*-deuteriated 2-propanol; thus, deuterium incorporation has been found to take place in both radicals.[45]

In regard to cyclopentadienyl derivatives, the reaction of ethyl radicals—generated by heating diethylmercury—with ferrocene[46] and the formation of cyclopentadienyl radicals from substituted dicyclopentadienylmercury[47] have been studied. On the other hand, benzyl radicals—obtained by pyrolysis or photolysis of dibenzylmercury—have been used for trapping of nitrogen-[48,49] and phosphorus-containing[50] radicals.

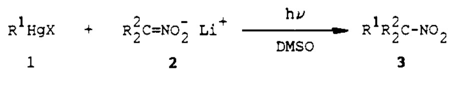
SCHEME 3[51]



SCHEME 4[53,54]



SCHEME 5[57,58]



The addition of dialkylmercury compounds to tetracyanoethylene (TCNE) through a charge-transfer mechanism, which involves two radicals has been described (Scheme 3).[51]

When the thermal or photochemical decomposition of the mercurial is performed in the presence of carbon tetrachloride as a solvent, olefins and alkyl chlorides are obtained as reaction products through a chain radical process.[52-54] Scheme 4 shows two examples as well as the proposed mechanism; when the alkyl substituents contain deuterium atoms at the β-position with respect to the mercury atom, an isotopic effect of 4.9 ± 0.1 (K_H/K_D) is observed.[53]

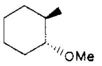
The above-described reaction has also been performed in the presence of perchloroethane;[55] in both cases an in-depth mechanistic study relating the reaction conditions, structure of reagents, initiators, etc. has been carried out, concluding that both processes are mechanistically similar. Finally, the spontaneous decomposition of di-*tert*-butylmercury in carbon tetrachloride has been demonstrated to occur via a radical mechanism.[56]

C. Photochemically Generated Radicals

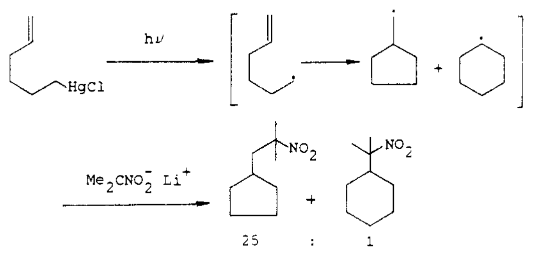
The photochemically induced reaction of different primary or secondary alkylmercury chlorides or bromides 1 with several anions derived from nitro derivatives 2 leads to the corresponding products 3 through an $S_{RN}1$ type mechanism (Scheme 5 and Table 1).[57,58]

The process is inhibited with di-*tert*-butyl nitroxide, it does not occur in the dark, and the reaction works only when the solvents are completely deoxygenated. Additional evidence for a radical mechanism is the

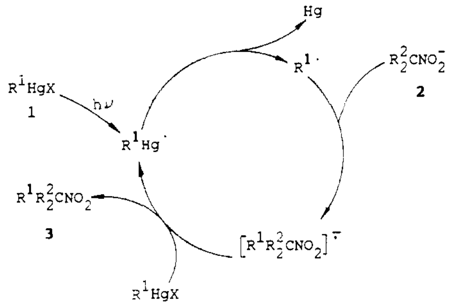
TABLE 1. Nitro Derivatives 3 from Organomercurials 1 and Nitronate Salts 2[57,58]

organomercurial 1		nitronate salt 2	nitro derivative 3
R^1	X	R^2_2	yield, %
$\overline{(CH_2)_4COCH}$	Cl	Me_2	56
	Br	Me_2	68
	Cl	$(CH_2)_5$	60
$PhCH_2$	Cl	$(CH_2)_5$	87
	Cl	Me_2	100
n-C_6H_{13}	Cl	Me_2	90
	Br	Me_2	50
c-C_6H_{11}	Cl	Me_2	76
	Cl	$(CH_2)_5$	84
i-Pr	Cl	Me_2	63
$CH_2{=}CHCH_2$	Cl	Me_2	50
	Cl	Me_2	14.5
c-$C_5H_9CH_2$	Cl	Me_2	35
Me	Cl	Me_2	2
t-Bu	Cl	Me_2	0
Ph	Cl	Me_2	0
(E)-$Me_3CCH{=}CH$	Cl	Me_2	0
2-$CH_2{=}CHCH_2OC_6H_4$	Cl	Me_2	0

SCHEME 6[58,59]



SCHEME 7[57,58]



SCHEME 8[60,61]

$$t\text{-BuHgCl} + Nu^- \xrightarrow[18\text{-crown-6}]{h\nu} t\text{-BuNu}$$

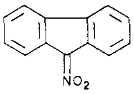
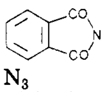
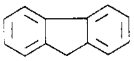
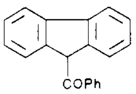
4

above-described reaction (Scheme 5) starting from (5-hexenyl)mercury chloride: the result of this process is a mixture of the corresponding cyclization products through the initially generated radical (Scheme 6).[59] The proposed mechanism is shown in Scheme 7.[57,58]

As shown in Table 1, the reaction does not work when a tertiary organomercurial (i.e., *tert*-butyl) or arylmercury chloride is used. However, this problem can be overcome in the case of the *tert*-butyl mercurial by carrying out the reaction in the presence of a stoichiometric amount of 18-crown-6 (Scheme 8 and Table 2).[60,61]

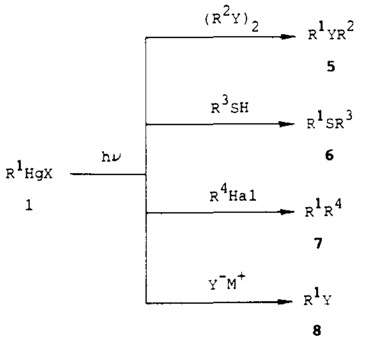
The photochemically generated radicals from organomercurials 1 have been used with success to produce coupling reactions with heteroatoms, yielding carbon–heteroatom bond formation.[62,63] The products 5–8 obtained in this way are listed in Scheme 9 and Table 3.

TABLE 2. Coupling Products 4 from t-BuHgCl and Nucleophiles Nu^-[60,61]

nucleophile Nu[a]	product 4 yield, %	ref
NO_2	71	60, 61
Me_2CNO_2	69	60, 61
$MeCHNO_2$	74	60, 61
CH_2NO_2	68	60, 61
$PhCHNO_2$	71	60, 61
$PhC(Me)NO_2$	67	60, 61
	0	60
$(O_2N)_2CNO_2$	0	60
	72	60, 61
N_3	34	60, 61
PhCHCN	4	60, 61
Ph_2CCN	48	60, 61
Ph_3C	39	60, 61
Ph_2CH	36	60, 61
Ph_2CCO_2Et	0	60
$Ph_2CCOCMe_3$	6	60
	44	60, 61
$PhC(CO_2Et)_2$	43	60, 61
$CH(CO_2Et)_2$	<2	60
$MeC(CO_2Et)_2$	<2	60
t-$BuCOCH_2$	7	60, 61
t-$BuCOCPh_2$	6	61
$PhCOCH_2$	54	60, 61
$PhCOCMe_2$	21	60, 61
PhCOCHMe	34	60, 61
PhCOCHPh	63	60, 61
$PhCOCPh_2$	57	60, 61
	8	60, 61
PhCOCHCOPh	2	60
PhCOC(Ph)COPh	3	60
PhCOCHCN	2	60
$PhCOCHCO_2Et$	2	60

[a] In all cases the potassium salt is used.

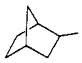
SCHEME 9[62,63]



As shown in Table 3, when (5-hexenyl)mercury chloride is used as starting material, a mixture of products is obtained arising from the corresponding 5-hexenyl and the equilibrated cyclopentylmethyl radical intermediates. The proposed mechanism for products 5 and 6 is included in Scheme 10.

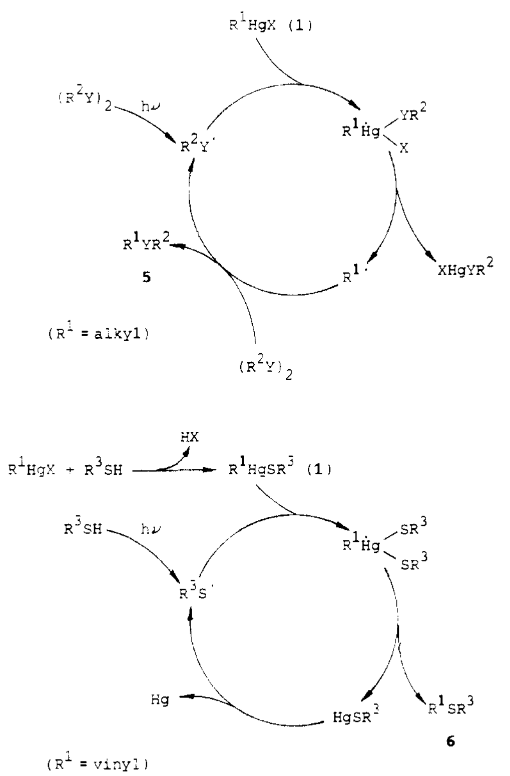
Radicals photochemically generated from organomercurials 9 can be added to olefins 10, yielding the corresponding coupling products 11 through a nonstereospecific chain radical process (Scheme 11 and Table 4).[64]

TABLE 3. Coupling Products 5–8 from Mercurials 1 and Reagents $(R^2Y)_2$, R^3SH, R^4Hal, and Y^-M^+ [62,63]

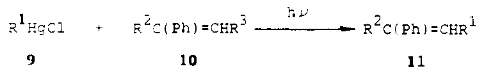
organomercurial 1		reagent				products 5–8	
R^1	X	R^2Y	R^3	R^4Hal	Y^-M^+	yield, %	ref
(*E*)-$Me_3CCH{=}CH$	Cl	*n*-BuS				100	62
		PhS				100	62
		PhSe				95	62
		PhTe				29	62
				$PhSO_2Cl$		84	62
					$(EtO)_2POK$	76	62
					PhP(OBu)OK	84	62
					p-$MePhCO_2Na$	81	62
					n-$PrSO_2Na$	75	62
			Ph			99	62
			t-Bu			100	62
			$PhCH_2$			64	62
(*Z*)-$HOCH_2C(Cl){=}CH$	Cl		Ph			61	62
$CH_2{=}CH$	Cl		Ph			100	62
		PhSe				91	62
(*E*)-EtC(OAc)=CEt	Cl		Ph			92	62
(*E*)-$Me_3CCH{=}CH$	AcO		Ph			100	62
			$PhCH_2$			97	62
$Ph_2C{=}CH$	Br	MeS				100	62
					p-$MePhSO_2Na$	61	62
				Me_2CHI		50	62
(*E*)-$Me_3CCH{=}CH$	PhS					99[a]	62
	n-BuS					100[a]	62
$Ph_2C{=}CH$	PhS					100[a]	62
$Ph_2C{=}CMe$	PhS					100[a]	62
(*E*)-PhCH=CH	PhS					100[a]	62
(*E*)-*n*-PrCH=CH	PhS					100[a]	62
	Cl				$(EtO)_2POK$	56	62
					p-$MePhSO_2Na$	71	62
(*E*)-PhCH=CH	Cl				*p*-$MePhSO_2Na$	21	62
			n-Bu			100	62
$CH_2{=}CHCH_2CH_2$	Cl	PhS				92	63
		PhSe				85	63
		PhTe				92	63
					p-$MePhSO_2SePh$	87[a]	63
$CH_3(CH_2)_4CH_2$	Cl	PhS				78	63
		PhSe				82	63
		PhTe				83	63
					p-$MePhSO_2SePh$	82[a]	63
				$PhSO_2Cl$		46	63
				CCl_3Br		56	63
t-$BuCH_2$	Cl	PhS				74	63
		PhSe				86	63
		PhTe				78	63
					p-$MePhSO_2SePh$	75[a]	63
i-Pr	Cl	PhS				100	63
		PhSe				100	63
c-C_6H_{11}	Cl	PhS				65	63
		PhSe				72	63
c-$C_5H_9CH_2$	Cl	PhS				86	63
		PhSe				84	63
	Br	PhS				43	63
		PhSe				53	63
		PhTe				45	63
					p-$MePhSO_2SePh$	48[a]	63
$CH_2{=}CH(CH_2)_3CH_2$	Cl	PhS				88[b]	63
		PhSe				93[b]	63
		PhTe				85[b]	63
					p-$MePhSO_2SePh$	81[a,b]	63
				$PhSO_2Cl$		54[b]	63
			Ph			58[b]	63
$PhCH_2$	Cl	PhS				15	63
		PhSe				72	63
		PhTe				80	63
					p-$MePhSO_2SePh$	68[a]	63
	$PhCH_2$	PhS				8	63
		PhTe				100	63
n-Bu	Cl	PhS				85	63
	n-Bu	PhS				100	63

[a] Product of the type 5 is isolated. [b] Mixture of the cyclopentylmethyl and Δ^5-hexenyl derivatives in different ratios depending on the reaction conditions.

SCHEME 10[62,63]

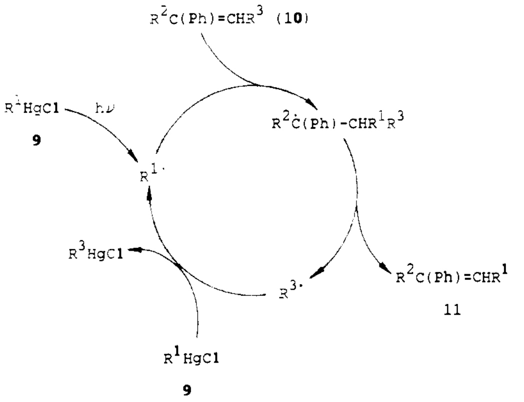


SCHEME 11[64]



$$\underset{9}{R^1HgCl} + \underset{10}{R^2C(Ph)=CHR^3} \xrightarrow{h\nu} \underset{11}{R^2C(Ph)=CHR^1}$$

SCHEME 12[64]



The proposed mechanism for the reaction described in Scheme 11 is indicated in Scheme 12.[64]

The corresponding photostimulated addition to diarylethenes **12** has been studied when in the starting organomercurial **9** (R^1 = *t*-Bu),[65] taking into account the influence of the substituents in the aryl groups. Thus, for X = H a 1:1 mixture of the products **13** and **14** is obtained, the mechanism being not a chain radical one. However, for X = OMe the major product is **13**, and for X = NO_2 the major product is **14**; in these cases a chain radical mechanism has been proposed (Scheme 13).[65]

Recently, the photochemically induced addition of cyclohexylmercury chloride (**9** with R^1 = c-C_6H_{11}) to different substituted olefins **15** has been described.[66] The process, which leads to the products **16**, takes place with partial retention in the configuration, and the highest stereospecificity has been found for R^2 = I in the olefin **15** (Scheme 14 and Table 5) .

TABLE 4. Olefins 11 from Organomercurials 9 and Alkenes 10[64]

organomercurial 9 R^1	reagent 10[a] R^2	R^3	product 11[b] yield, %
i-Pr	H	*n*-Bu_3Sn	86
	H	HgCl	83
	H	I	76
	H	$PhSO_2$	68
	H	PhSO	20
	H	PhS	35
	Ph	*n*-Bu_3Sn	73
	Ph	HgBr	96
	Ph	I	89
	Ph	$PhSO_2$	87
	Ph	PhS	55
t-Bu	H	*n*-Bu_3Sn	83
	H	HgCl	40
	H	$PhSO_2$	43
	H	PhSO	32
	Ph	*n*-Bu_3Sn	78
	Ph	HgBr	100
	Ph	I	86
	Ph	$PhSO_2$	88
n-Bu	H	*n*-Bu_3Sn	46
	H	I	22
$CH_2CH(CH_2)_4$	H	*n*-Bu_3Sn	55[c]
c-$C_5H_9CH_2$	H	*n*-Bu_3Sn	52[c]
$CH_2{=}CH(CH_2)_2$	H	*n*-Bu_3Sn	45
$(EtO)_2PO$[d]	H	HgCl	65
	H	I	85
	Ph	*n*-Bu_3Sn	65
	Ph	HgBr	85
	Ph	I	86
PhS[d]	H	I	97
	Ph	I	100
$PhSO_2$[d]	Ph	HgBr	100
$PhCOCH_2$[d]	Ph	HgBr	64

[a] The compounds **10** with R^2 = H have the *E* configuration. [b] The products **11** with R^2 = H appear as an *E*/*Z* mixture. [c] The only reaction product is the cyclopentylmethyl derivative. [d] The organomercurial $R^1{}_2Hg$ is used.

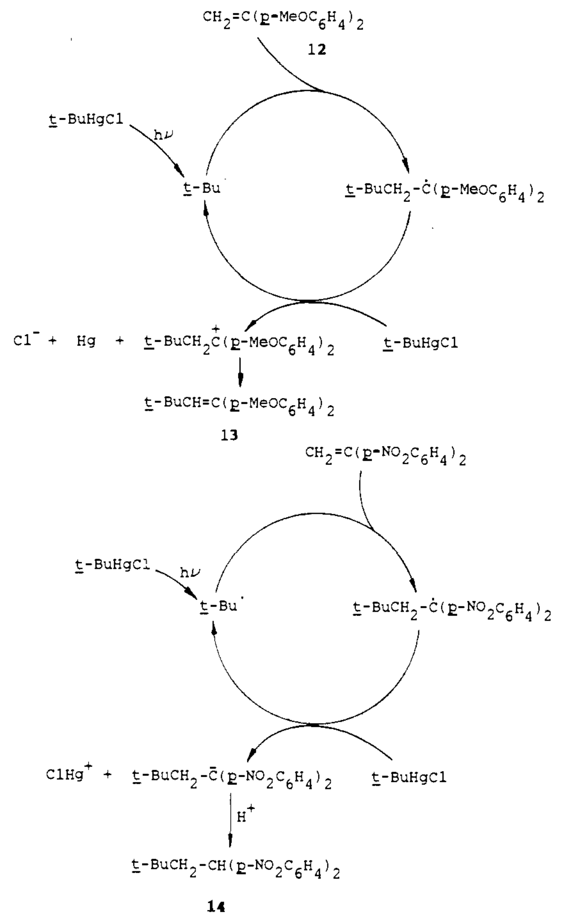
TABLE 5. Olefins 16 from Cyclohexylmercury Chloride and Alkenes 15[66]

reactant 15 stereochemistry	X	R^2	product 16 yield, %	*E*/*Z* ratio
E	CO_2Me	*n*-Bu_3Sn	20	36
Z	CO_2Me	*n*-Bu_3Sn	34	2.5
E	CO_2Me	*n*-Bu_3Sn	66	23
Z	CO_2Me	*n*-Bu_3Sn	70	2.1
E	CO_2Me	I	34	20
Z	CO_2Me	I	45	0.9
E	HgCl	Cl	28	4.3
Z	HgCl	Cl	39	0.7
Z	Cl	Cl	70	0.8
E	Cl	Cl	63	0.7

The former results can be explained admitting that, in the case of a secondary organomercurial such as cyclohexylmercury chloride, the elimination of group X is faster than the establishment of equilibrium between I and II (Scheme 15).[66] When instead of the cyclohexyl group a more bulky one, such as *tert*-butyl, is present in the mercurial **1**, the Ib configuration is very disfavored and the elimination step takes place through the configuration IIb (Scheme 15).[66]

The addition of radicals—photochemically generated from organomercurials **1**—to pyridine constitutes an adequate method for radical alkylation of systems of this type.[67,68] The reaction can be carried out either by starting from the isolated organomercurial **1** or in situ starting from olefins and performing previous meth-

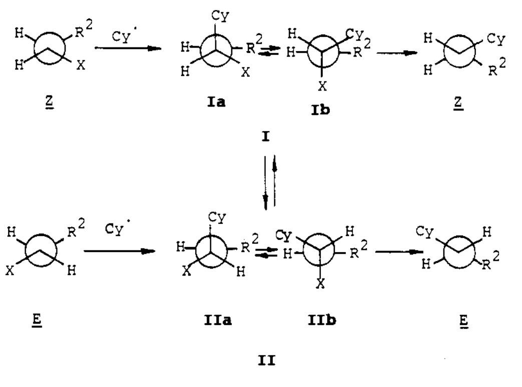
SCHEME 13[65]



SCHEME 14[66]

$$\underset{\mathbf{15}}{c\text{-}C_6H_{11}HgCl} + XCH{=}CHR^2 \xrightarrow{h\nu} \underset{\mathbf{16}}{c\text{-}C_6H_{11}CH{=}CHR^2} + XHgCl$$

SCHEME 15[66]



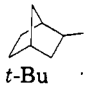
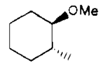
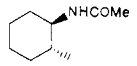
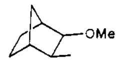
(Cy = c-C6H11)

oxymercuration with mercury trifluoroacetate in methanol (Scheme 16 and Table 6).

The above-described reaction (Scheme 16) has been extended to other systems such as substituted pyridines or *N,N,N′,N′*-tetramethyl-*p*-phenylendiamines.[67,68]

The reaction of photochemically generated radicals—from organomercury compounds—with olefins or aromatic compounds has been applied to phenylacetylenes **18** bearing another substituent such as iodine, phenylmercapto, phenylsulfonyl, or a mercury or a tin atom; therefore, products **19** are prepared in this way (Scheme 17 and Table 7).[69]

TABLE 6. Alkylated Pyridines 17 from Organomercurials 1 and Pyridine[68]

organomercurial 1		product 17	
R	X	yield, %	*o*/*p* ratio
Et	Cl	64	2.0
n-Bu	Cl	66	2.4
n-C_6H_{13}	Cl	83	*a*
t-$BuCH_2CH_2$	Cl	64	2.5
t-$BuCH_2$	Cl	54	1.9
c-$C_5H_9CH_2$	Cl	77	1.9
i-Pr	Cl	72	1.6
c-C_6H_{11}	Cl	69	3.1
	Cl	90	4.1
t-Bu	Cl	94	1.4
$MeOCH_2CH_2$	CF_3CO_2	73	2.0
$MeOCH(Me)CH_2$	CF_3CO_2	76	2.5
$MeOCH(Et)CH_2$	CF_3CO_2	78	2.5
$MeOCH(n$-$Bu)CH_2$	CF_3CO_2	80	2.7
$MeOCH(t$-$Bu)CH_2$	CF_3CO_2	67	2.8
$MeOCH(Me)CH(Me)$	CF_3CO_2	81	1.9
	CF_3CO_2	86	2.2
	CF_3CO_2	69	2.3
	CF_3CO_2	78	3.0

[a] Not given.

TABLE 7. Acetylenes 19 from Organomercurials 9 and Substituted Phenylacetylenes 18[69]

organomercurial 9 R	acetylene 18 X	product 19 yield, %
t-Bu	I	100
c-C_6H_{11}	I	93
n-Bu	I	48
$(EtO)_2PO$	I	32
i-Pr	$PhSO_2$	44
c-C_6H_{11}	$PhSO_2$	67
t-Bu	$PhSO_2$	55
$(EtO)_2PO$	$PhSO_2$	30
i-Pr	PhS	42
c-C_6H_{11}	PhS	46
t-Bu	PhS	44
n-Bu	$PhC{\equiv}CHg$	9
c-C_6H_{11}	$PhC{\equiv}CHg$	26
t-Bu	$PhC{\equiv}CHg$	34
$(EtO)_2PO$	$PhC{\equiv}CHg$	61
n-Bu	n-Bu_3Sn	13
c-C_6H_{11}	n-Bu_3Sn	43
t-Bu	n-Bu_3Sn	61

SCHEME 16[67,68]

$$\underset{\mathbf{1}}{RHgX} + C_5H_5N \xrightarrow{h\nu} \underset{\mathbf{17}}{RC_5H_4N}$$

SCHEME 17[69]

$$\underset{\mathbf{9}}{RHgCl} + \underset{\mathbf{18}}{PhC{\equiv}CX} \xrightarrow{h\nu} \underset{\mathbf{19}}{PhC{\equiv}CR}$$

The relative reactivity of acetylenes **18** with cyclohexylmercury chloride is as follows: X = $PhSO_2$ (65) > I (19) > n-Bu_3Sn (1.0), the mechanism being similar to that described for the radical reaction with substituted olefins.

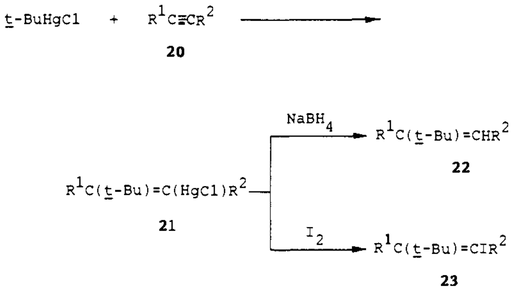
Recently, the photostimulated radical addition of *tert*-butylmercury chloride to acetylenes **20**, which bear electron-withdrawing groups, has been described,

TABLE 8. Olefins 22 and 23 from *tert*-Butylmercury Chloride and the Acetylenes 20[70]

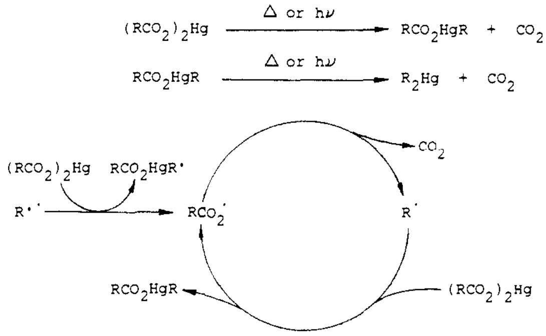
acetylene 20		product,[a] yield, %	
R^1	R^2	22	23
H	Ph	63	41
H	COMe	90	85
CO_2Et	Ph	72	94
CO_2Et	CO_2Et	97	96

[a] Mixture of Z/E isomers.

SCHEME 18[70]



SCHEME 19[73]



yielding vinyl mercurials 21;[70] these organomercurials are transformed in situ into the corresponding reduced or iodinated systems 22 and 23, respectively (Scheme 18 and Table 8).[70]

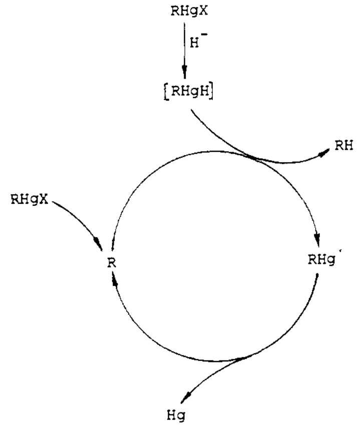
Finally, the photochemical decomposition of organomercurials bearing carboxymethyl groups leads to carboxymethyl radicals; the results, depending on the solvent used (benzene[71] or tetrahydrofuran[72]), yield different reaction products.

D. Heteroradicals

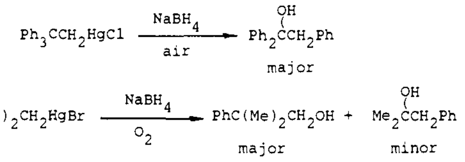
By thermal or photochemical decomposition of mercury carboxylates—either isolated or generated in situ by reaction of the corresponding alkaline carboxylates with mercury acetate—can be transformed, depending on the reaction conditions and the groups R, into mercurials arising from a mono- or didecarboxylation. The proposed mechanism includes the formation of an oxygenated radical of the type $RCO_2^\bullet$ as is shown in Scheme 19.[73] The same reaction is also known for sulfinic acid derivatives.[74] However, a similar radical mechanism in this case has not been postulated.

A convenient method for generating bis(trifluoromethyl) nitroxide radicals is to heat mercury bis(trifluoromethyl)nitroxide at 85 °C;[75,76] this radical has been used in the synthesis of new organic and inorganic compounds, as well in the trapping of other radicals.[77]

SCHEME 20



SCHEME 21[84,85]



Silyl radicals have been generated from bis(trimethylsilyl)mercury, and they have been used, for instance, in the silylation of aromatic systems such as substituted pyridines.[78,79] The reaction of bis(trimethylsilyl)mercury or the ethyl derivative with pyridines bearing a metal like silicon, germanium, tin, or lead,[80] arenes like benzene or toluene,[81] and alkyl or acyl chlorides[82] has also been studied. In all cases a trimethylsilyl radical has been proposed as a reaction intermediate. In a similar way, the reaction of bis(trialkylgermanyl)mercury with aromatic compounds such as naphthalene, anthracene, or anisole,[81] pyridine,[80] and alkyl or aryl chlorides[82] through the corresponding germanyl radicals has been studied.

Finally, compounds containing a mercury–tin bond have been used for generating stannyl radicals, which are adequate precursors for compounds with tin–tin bonds.[83]

III. Radicals Generated by Means of Hydrides

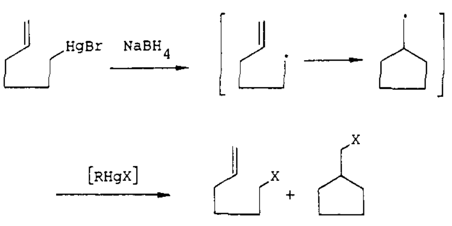
A. Radical Mechanism in the Reduction of Organomercurials with Hydrides

The reduction of organomercury compounds by means of metal hydrides, especially sodium borohydrides, has widely been studied from a mechanistic point of view, the mechanism being of a chain radical type (Scheme 20).

The intermediates have been trapped by carrying out the reaction in the presence of air;[84,85] in these cases, together with the expected oxygenated products, others, arising from a transposition process of the initially generated radical, are obtained (Scheme 21).

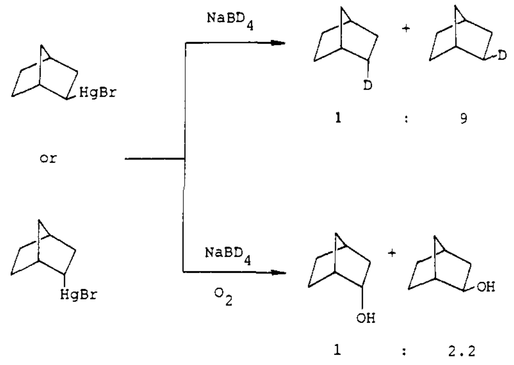
Furthermore, the reduction of (5-hexenyl)mercury bromide with sodium borohydride leads to the expected products coming from the initially formed radical; on the other hand, the use of sodium borodeuteride instead of the corresponding hydride indicates an isotopic effect, which is based on the influence of winning a hydrogen or a deuterium atom for the radical intermediate from the species RHgX (X = H or D) (Scheme 22).[86,87]

SCHEME 22[86,87]

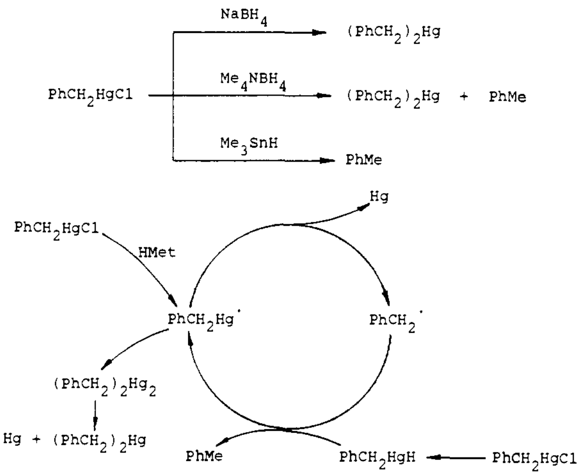


(X = H or D)

SCHEME 23[91]



SCHEME 24[93]



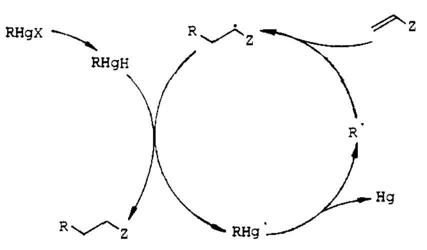
However, the most important contribution to the radical mechanism in the hydride-promoted reduction of organomercurials is in relation to stereochemical studies.[88-92] Thus, for instance, in the reduction with sodium borodeuteride or in the reduction/oxidation of both isomers of norbornylmercury bromide, the same mixture of products was obtained, with loss in the initial stereochemistry (Scheme 23).

When the generated radical is especially stable, for instance the benzyl radical, the obtained products depend on the hydride used, the reduction competing with the symmetrization reaction. In Scheme 24 the proposed mechanism for these processes is included.[93]

A similar radical mechanism to that described above has been proposed for the reduction with other reducing agents such as tin hydrides,[93-95] lithium aluminum hydride,[96] or lithium naphthalenide.[97] In regard to the starting organomercurials, they can either lack functionality or be β-substituted.[98,99]

In subsections C of this section, the synthetic potential of radicals from the hydride reduction of organomercurials is discussed.

SCHEME 25[11]



B. Theoretical Comments and Selectivity

The generation of radicals starting from organomercurials by means of metal hydrides, mainly sodium borohydride, together with their further use in the formation of carbon–carbon bonds by reaction with electron-poor alkenes has been called "the mercury method" (Scheme 25).[11] This methodology has extensively been studied from a theoretical point of view.[14]

Thus, the 5-hexenyl radical is easily generated from the corresponding mercurial, and it cyclizes to form the cyclopentylmethyl radical; the relative reaction rate of the both species with an alkylmercury hydride or an electrophilic olefin—i.e., acrylonitrile or methyl acrylate—in a competition experiment has been investigated: the mentioned radicals are trapped by the hydride with a rate greater than 10^7 L·M^{-1}·s^{-1}.[100]

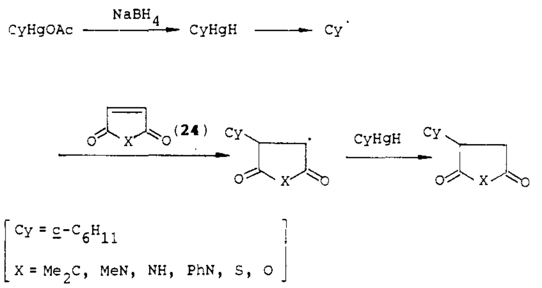
When the kinetics of the reaction between different primary, secondary, or tertiary radicals with several electrophilic olefins was studied, it was found that the radicals behave as nucleophiles, and the reactivity increases as follows: primary < secondary < tertiary.[101,102] In the case of the cyclohexyl radical, an involved study was carried out considering the effect of the substituents of the electrophilic olefin on the reaction rate,[103-105] finding interesting correlations between the rate constant and the electronic effect of the substituent in the electron-poor alkene. This study has also been extended to α- and β-functionalized radicals; in this case the steric effects play an important role in the reaction rate.[106]

Especially interesting is the kinetics in the reaction of radicals generated by "the mercury method" with substituted styrenes:[107,108] an important correlation between the reaction rate constant and the corresponding σ values is found for the aromatic ring substituents.

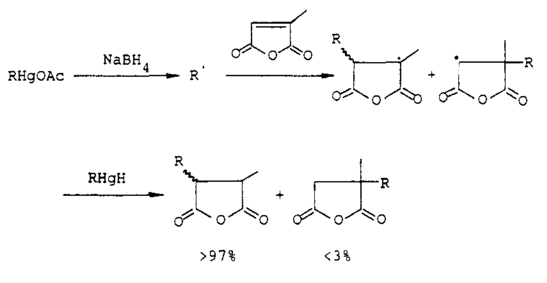
Upon comparison of "σ radicals" (an unpaired electron in an sp^3 orbital) and "π radicals" (an unpaired electron in a p orbital) generated by the above-mentioned method, it was found that the former are as selective as the latter in the reaction with different electron-poor olefins.[109,110] The chemoselectivity of several σ- and π-radicals with the halogens chlorine and bromine in a mixture of carbon tetrachloride/bromotrichloromethane was explored; in general, the selectivity is drastically dependent on the temperature and steric effects: at 273 K the methyl radical is the least selective of the series, while at 403 K it appears as the most selective.[111,112]

Numerous studies have been carried out concerning the selectivity of different radicals prepared from organomercurials and sodium borohydride with electrophilic olefins. Thus, it has been shown that the trans-disubstituted olefins of the type YCH=CHCO$_2$R

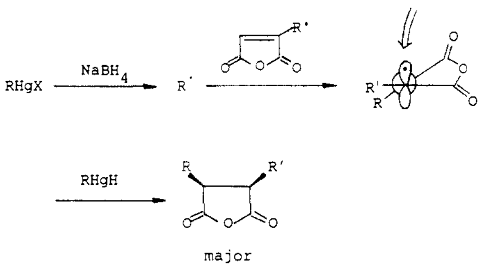
SCHEME 26[114]



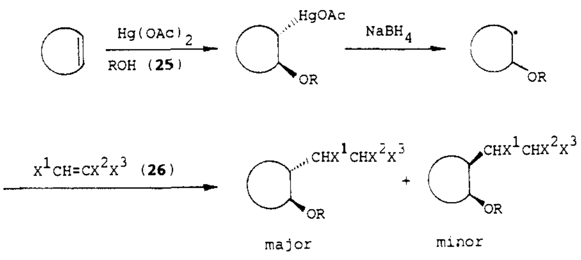
SCHEME 27[115]



SCHEME 28[116,117]



SCHEME 29[118]



27 28

react more rapidly than the cis isomer, this "cis effect" increasing with the size of the group Y.[113] In the reaction of cyclohexyl radicals with systems of the type 24, it has been pointed out that the relative rate increases as follows: $Me_2C > MeN > NH > PhN > S > O$ (Scheme 26).[114]

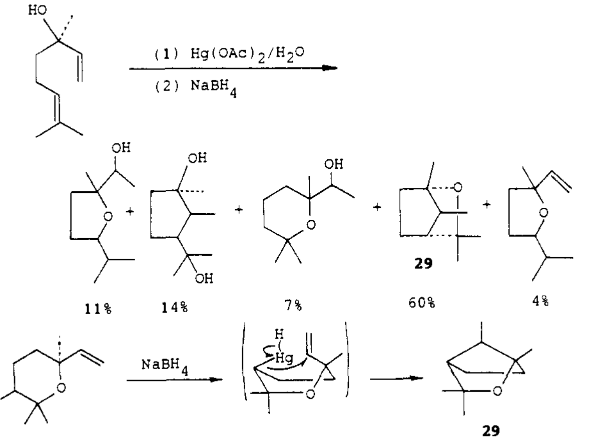
The regioselectivity in the addition process of primary, secondary, or tertiary radicals to 2-methylmaleic anhydride shows that, in any case, the major reaction product is α,α′-disubstituted (Scheme 27).[115] In relation to the stereochemistry of the reaction mentioned in Scheme 27, it has been observed that the major diastereoisomer has both substituents in the cis position (anti attack of RHgH). The selectivity is considerably increased with the bulkiness of the generated radical R·. This can be easily explained by considering that the attack of the alkylmercury hydride takes place preferentially on the opposite side of where the alkyl group in the α-position of maleic anhydride is attached (Scheme 28).[116,117]

TABLE 9. Diastereoisomers 27 and 28 from Cyclic Olefins, Alcohols 25, and Electrophilic Olefins 26[118]

	alcohol 25	olefin 26			product 27 + 28[a]	
cyclic olefin	R	X^1	X^2	X^3	yield, %	27/28 ratio
cyclopentene	Et	CN	H	CN	60	60/40
		H	Cl	CN	66	72/28
		H	H	CN	65	71/23
		H	Me	CN	46	77/23
		H	H	COMe	51	87/13
		H	H	CO$_2$Me	60	88/12
		H	H	Ph	15	90/10
	Me	H	H	CN	65	78/22
	i-Pr	H	H	CN	50	77/23
	t-Bu	H	H	CN	8	80/20
dihydrofuran	Me	CN	H	CN	20	64/36
		H	H	CN	45	86/14
		H	H	COMe	40	88/12
		H	H	CO$_2$Me	48	93/7
cyclohexene	Me	H	H	CN	67	65/35
		H	H	CO$_2$Me	65	70/30
		H	H	Ph	12	75/25
dihydropyran	Me	CN	H	CN	69	58/42
		H	H	CN	76	66/34
		H	H	COMe	68	73/27
		H	H	CO$_2$Me	64	75/25

[a] Overall yield for the one-pot reaction.

SCHEME 30[120]



Finally, the diastereoselectivity in the addition of cyclic β-substituted radicals, generated by solvomercuration–reduction of cyclic olefins such as cyclopentene, 2,3-dihydrofuran, cyclohexene, and 2,3-dihydropyran, to electrophilic olefins has been described. In all cases the trans diastereoisomer turned out to be the major one (Scheme 29 and Table 9).[118]

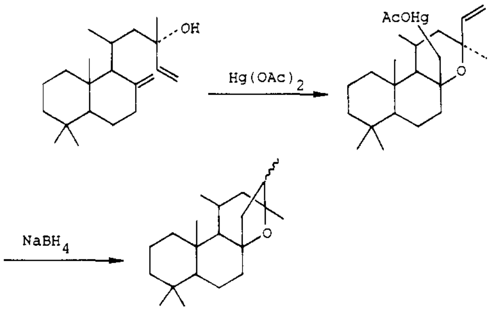
Recently, the mechanism of the 1,2-migration of vinyl or formyl substituents in free radicals generated via a mercuration–reduction tandem reaction was studied from a theoretical point of view.[119]

C. Applications in Organic Synthesis

1. Intramolecular Reaction with Olefins

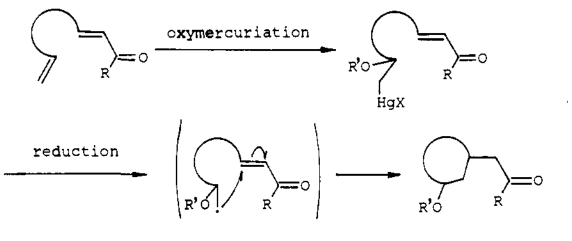
Linalool undergoes cyclization through the tandem oxymercuration–reduction to give a complex mixture of products, where the major one (29) is probably formed by a radical mechanism via the corresponding

SCHEME 31[120]

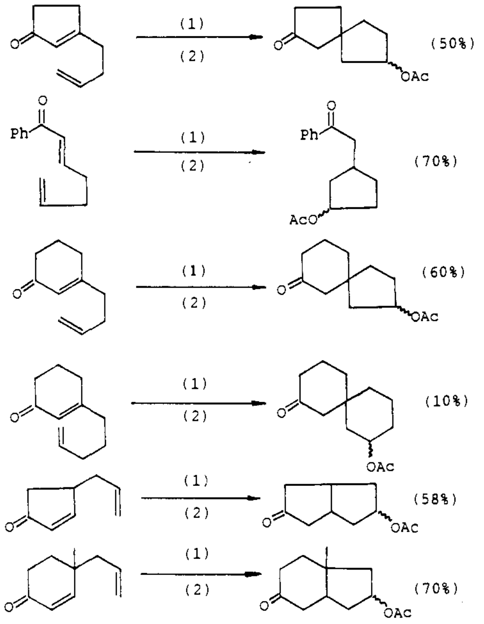


30

SCHEME 32[121]

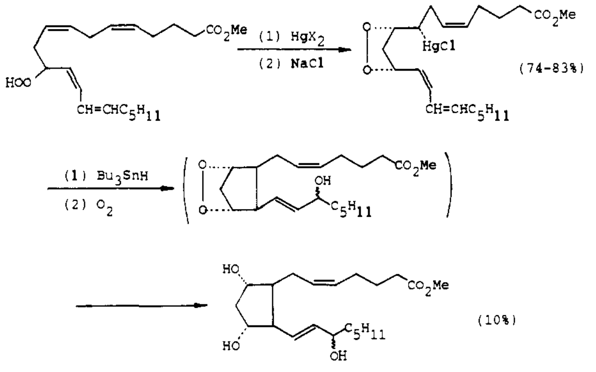


SCHEME 33[121]

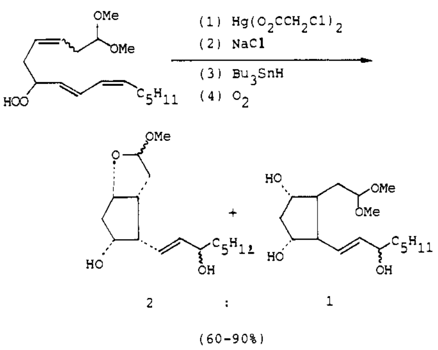


[(1) $Hg(OAc)_2/HOAc$; (2) $NaBH(OMe)_3$]

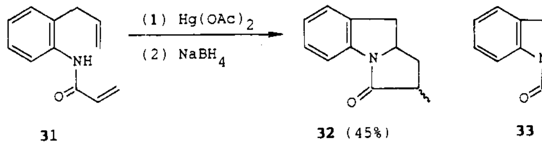
SCHEME 34[122]



SCHEME 35[123]



SCHEME 36[124]



31 32 (45%) 33

SCHEME 37[125]

$$\underset{\mathbf{34}}{R^1HgOAc} + \underset{\mathbf{26}}{X^1CH{=}CX^2X^3} \xrightarrow{NaBH_4} \underset{\mathbf{35}}{R^1X^1CH\text{-}CHX^2X^3}$$

mercury hydride intermediate (Scheme 30). However, it has not been possible to trap the corresponding radical by reaction with oxygen.[120] The same principle has been used to prepare the strobane structure **30** from epimanool via mercuration–reduction (Scheme 31).[120]

The intramolecular formation of monocyclic spiranic systems has been described as shown in Scheme 32. Some examples of this strategy are included in Scheme 33.[121]

The reduction step can also be carried out by using tributyltin hydride, and the resulting radical can be trapped with molecular oxygen. Thus, this sequence has successfully been used in a synthesis of prostaglandins (Schemes 34[122] and 35[123]).

In relation to intramolecular reactions with amino mercurials, the cyclization of the adduct **31** is known to give the product **32** (Scheme 36). In this reaction, which constitutes a reasonable alternative to the same process promoted by palladium, no isomer **33** was detected.[124]

2. Intermolecular Reaction with Olefins

In this section the intermolecular reaction of different unsubstituted and functionalized radicals—generated by reaction of organomercurials with sodium borohydride—with olefins will be considered.

(a) Unsubstituted Radicals. The reduction of different alkylmercury acetates **34** with sodium borohydride in the presence of electron-poor olefins **26** constitutes an adequate formation method for carbon–carbon bonds, yielding the corresponding coupling products **35** (Scheme 37 and Table 10).[125]

Starting organomercurials **34** are easily obtained from the corresponding organomagnesium compounds by reaction with mercury acetate.[3]

The reaction included in Scheme 37 fails when crotonic esters are used as electrophilic olefins. This problem has been overcome by employing 1,1-dicyano olefins **36**, as shown in Scheme 38. This procedure is a convenient route to β,β-disubstituted carboxylic acids **38** by final hydrolysis of the dicyano derivatives **37** (Table 11).[126]

The reaction mechanism included in Schemes 37 and 38 has already been described in Scheme 25.[11] The

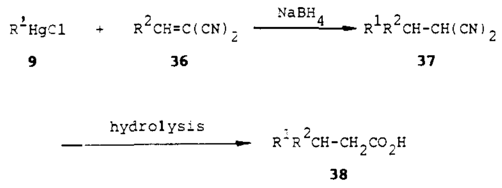
TABLE 10. Coupling Products 35 from Organomercurials 34 and Olefins 26[125]

organomercurial 34	olefin 26			product 35
R^1	X^1	X^2	X^3	yield, %
t-Bu	H	H	CO_2Me	83
	H	H	COMe	70
	H	H	Ph	15
	H	Me	CO_2Me	83
	Me	H	CO_2Me	<1
c-C_6H_{11}	H	H	CN	61
	H	H	CO_2Me	62
	H	H	COMe	70
	H	H	CHO	27
	H	H	Ph	45
	H	Me	CN	50
	H	Me	CO_2Me	84
	H	Cl	Cl	27
	Me	H	CN	53
	Me	H	CO_2Me	24
	CO_2Me	H	CO_2Me	34
	H	H	*n*-C_6H_{13}	2
	H	H	OEt	<2
n-C_6H_{13}	H	H	CO_2Me	64
	H	H	COMe	51
	H	H	Ph	20
	H	Me	CO_2Me	31
	Me	H	CO_2Me	49

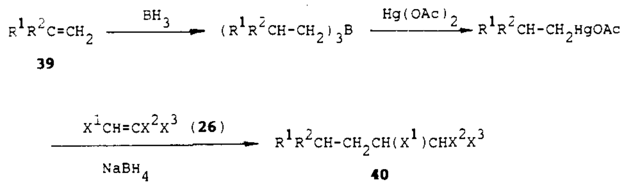
TABLE 11. Carboxylic Acids 38 from Organomercurials 9 and Dicyano Olefins 36[126]

organomercurial 9 R^1	dicyano olefin 36 R^2	product 38 yield, %
c-C_6H_{11}	Me	50
	n-Pr	45
	i-Pr	20
	i-Bu	45
t-Bu	Me	50

SCHEME 38[126]



SCHEME 39[129]



corresponding reduction products R^1H are obtained as byproducts in this process.

Another possibility of carrying out the coupling reaction of organomercurials and electrophilic olefins by generating the corresponding radicals consists in the formation of the starting mercurials by a tandem hydroboration[127]–mercuration[128] process as shown in Scheme 39 and Table 12.[129]

The method described in Scheme 39 can be considered a convenient procedure for coupling between electron-rich and electron-poor olefins.[129]

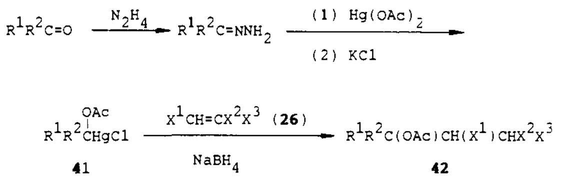
(b) α-Substituted Radicals. (α-Acetoxyalkyl)mercury chlorides 41 can be prepared from ketones via mercuration of the corresponding hydrazones.[130] When these organomercurials 41 are used in the coupling process with electrophilic olefins 26 in the presence of sodium borohydride, the corresponding products 42 are isolated (Scheme 40 and Table 13).[131-133]

TABLE 12. Coupling Products 40 from Olefins 39 and 26[129]

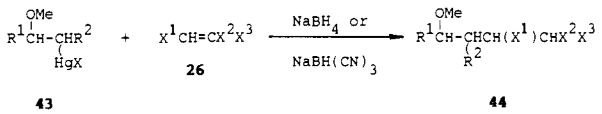
olefin 39		olefin 26			product 40
R^1	R^2	X^1	X^2	X^3	yield, %
H	*t*-Bu	H	H	CN	47
H	4-MeC_6H_4	H	H	CN	50
H	2-$AcOC_6H_4CH_2$	H	H	CN	65
H	2-$HOC_6H_4CH_2$	H	H	CN	48
H	$BrCH_2CH_2$	H	H	CN	53
H	$AcOCH_2$	H	H	CN	51
H	$TsOCH_2CH_2$	H	H	CN	71
H	$EtO_2C(CH_2)_8$	H	H	CN	57
H	EtO	H	H	CN	55
H	$PhOCH_2$	H	H	CN	55
Me	Et	H	H	CN	65
Me	*n*-Pr	H	H	CN	57
Me	$ClCH_2$	H	H	CN	50
	β-pinene	H	H	CN	53
H	c-C_6H_9[a]	H	H	CN	54
		H	H	CO_2Me	47
		H	H	COMe	44
		H	Cl	CN	52
		H	Cl	Cl	28
		H	Me	Ph	13
		CN	Me	CN	37
		OC–O–CO		H	53
		OC–NH–CO		H	50

[a] c-C_6H_9 = 3-cyclohexenyl.

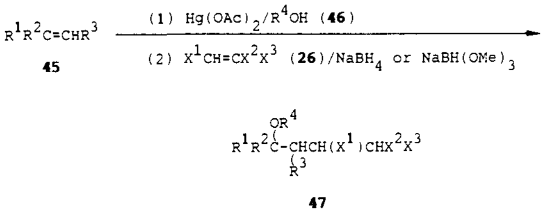
SCHEME 40[131-133]



SCHEME 41[134,135]



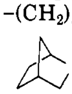
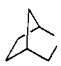
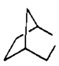
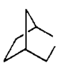
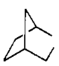
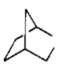
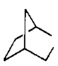
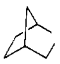
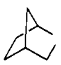
SCHEME 42[136,137]



The reaction indicated in Scheme 40 can be carried out without isolating the mercurial 41, in a one-pot process, the yields being lower in the in situ procedure due to the resulting byproducts and the necessary purification of the final products 42.[132]

The selectivity of α-acetoxyalkyl radicals has been investigated: when the groups R^1 and R^2 in the mercurial 41 are bulky, the reaction rate is lower with diethyl fumarate than with methyl acrylate.[106] Likewise, the relative nucleophilicity of different radicals of type 41 has been studied by using competition reactions with other primary, secondary, and tertiary radicals: the acetoxyalkyl radical turned out to be less nucleophilic than cyclohexyl radical, a logical consequence of the ability of the acetoxy group for attracting electrons.[133]

TABLE 13. Coupling Products 42 from Organomercurials 41 and Olefins 26[131-133]

organomercurial 41		olefin 26			product 42	
R^1	R^2	X^1	X^2	X^3	yield, %	ref
Me	Me	H	H	CN	70	131, 132
Me	Et	H	H	CN	65	131, 132
Me	*n*-Pr	H	H	CN	66	132
Me	*i*-Pr	H	H	CN	62	131
Me	*t*-Bu	H	H	CN	46	132
Et	Et	H	H	CN	71	131
i-Pr	*i*-Pr	H	H	CN	33	131
t-Bu	*t*-Bu	H	H	CN	<2	132
$-(CH_2)_4-$		H	H	CN	72	131
$-(CH_2)_5-$		H	H	CN	72	131
		H	H	CN	77	132
Me	COMe	H	H	CN	<2	132
Me	Ph	H	H	CN	<2	132
Me	Me	H	H	CO_2Me	68	132
$-(CH_2)_5-$		H	H	CO_2Me	55	132
		H	H	CO_2Me	75	132
$-(CH_2)_5-$		H	H	COMe	43	132
		H	H	COMe	58	132
Me	Me	H	H	Ph	13	132
$-(CH_2)_5-$		H	H	Ph	12	132
		H	H	Ph	17	132
$-(CH_2)_5-$		H	Me	CN	49	132
		H	Me	CN	58	132
Me	Me	H	Me	CO_2Me	23	133
		H	Me	CO_2Me	51	132
Me	Me	H	Cl	CN	72	132
		H	Cl	CN	70	132
$-(CH_2)_5-$		H	Cl	Cl	27	132
		H	Cl	Cl	31	132
Me	Me	CN	H	CN	76	132
$-(CH_2)_5-$		CN	H	CN	69	132
		CN	H	CN	52	132
Me	Me	CO_2Et	H	CO_2Et	54	132
$-(CH_2)_5-$		CO_2Et	H	CO_2Et	40	132
		CO_2Et	H	CO_2Et	61	132
		Me	H	CN	9	132
$-(CH_2)_5-$		OC–O–CO		H	75	132
		OC–O–CO		H	57	132
		CO_2Me	Me	CO_2Me	16	132
Me	Me	H	Cl	CO_2Me	54	133
		H	MeO	CO_2Me	5	133
		H	EtO	CO_2Et	52	133

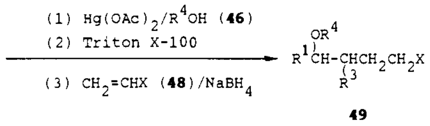
(c) β-Substituted Radicals. β-Oxygenated and β-nitrogenated organomercurials, which are the most important β-substituted mercurials, are precursors of the corresponding radicals and will be considered separately.

TABLE 14. Coupling Products 44 from Organomercurials 43 and Olefins 26[134,135]

organomercurial 43			olefin 26			product 44	
R^1	R^2	X	X^1	X^2	X^3	yield, %	ref
$-(CH_2)_3-$		Cl	H	H	CN	60	135
			H	H	CO_2Me	54	135
$-(CH_2)_4-$		Cl	H	H	CN	77	134
$-(CH_2)_4-$		Br	H	H	CN	66	135
$-(CH_2)_4-$		Cl	H	H	CO_2Me	50	134
$-(CH_2)_4-$		Br	H	H	CO_2Me	51	135
$-(CH_2)_4-$		Cl	H	H	Ph	22	134
			H	Me	CN	47	134
			H	Me	CO_2Me	38	134
			H	Cl	CN	65	134
			H	Cl	Cl	25	134
			CN	H	CN[a]	61	134
			CO_2Et	H	CO_2Et[a]	53	134
			CO_2Et	H	CO_2Et[b]	30	134
			Me	H	CN	8	134
			CO_2Et	Me	CO_2Et[a]	31	134
Ph	H	Cl	H	H	CN	53–60	134, 135
			H	H	CO_2Et	42–44	134, 135
			H	H	Ph	10	134
			H	Me	CN	43	134
			H	Me	CO_2Me	36	134
			H	Cl	CN	60	134
			CN	H	CN[a]	34	134
			CO_2Et	H	CO_2Et[a]	38	134
			CO_2Et	H	CO_2Et[b]	21	134
			Me	H	CN	6	134
			CO_2Et	Me	CO_2Et[a]	22	134
$n-C_6H_{13}$	H	Br	H	H	CN	57	135
$PhCH_2$	H	Cl	H	H	CN	55	135
			H	H	CO_2Et	46	135
Ph	Me	Cl	H	H	CN	46	135

[a] The CN or CO_2Et groups are in a trans position. [b] The CN or CO_2Et groups are in a cis position.

SCHEME 43[135]



$$R^1CH{=}CHR^3 \xrightarrow[\text{(3) } CH_2{=}CHX\ (\mathbf{48})/NaBH_4]{\text{(1) } Hg(OAc)_2/R^4OH\ (\mathbf{46})\quad \text{(2) Triton X-100}} R^1CH(OR^4){-}CH(R^3)CH_2CH_2X$$

(i) β-Oxygenated Radicals. The reaction of different (β-alkoxyalkyl)mercury compounds **43**, obtained by solvomercuration of the corresponding olefins[1-8] with electron-poor alkenes **26** in the presence of sodium borohydride or trimethoxyborohydride, gives the expected coupling products **44** (Scheme 41 and Table 14).[134,135]

The reaction described in Scheme 41 can be carried out in situ, without isolating the intermediate mercurials **43**; so, the starting materials are the corresponding olefins **45** (Scheme 42 and Table 15).[136,137]

The yields in the coupling reaction described in Scheme 42, for β-alkoxy as well as for β-hydroxy mercurials, can be notably improved by using sodium borohydride as a reducing agent when a surfactant is employed as a phase-transfer catalyst in the reduction step (Scheme 43 and Table 16).[135]

When mercuration is performed with an olefin that bears a nucleophilic group, an intramolecular addition can take place; the further coupling reaction with an electrophilic alkene in the presence of a hydride is exemplified in Scheme 44.[138]

The former process has been applied to 1,3-dienic systems **50** as starting educts for the mercuration step; the kinetically controlled mercuration leads to the

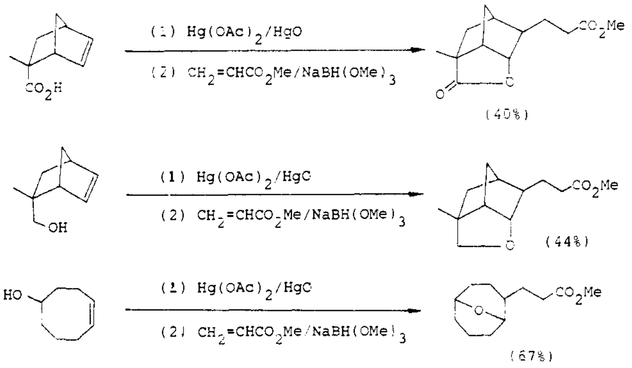
TABLE 15. Coupling Products 47 from Olefins 45 and 26 and Alcohols 46[136,137]

olefin 45			alcohol 46	olefin 26			product 47	
R^1	R^2	R^3	R^4	X^1	X^2	X^3	yield, %	ref
H	H	H	Me	H	H	CO_2Et	50	136
H	Me	Me	Et	H	H	CN	75	137
H	*n*-Bu	H	Me	H	H	CO_2Me	48	136
			Et	H	H	CN	65	137
H	Ph	H	Me	H	H	CO_2Me	50	136
			Et	H	H	CN	48	137
H	$-(CH_2)_3-$		Me	H	H	CO_2Me	65	136
			Et	H	H	CN	65	137
			Et	H	H	CO_2Me	60	137
			Et	H	H	Ph	15	137
			Et	H	Cl	CN	66	137
			Et	H	Cl	Cl	21	137
			Et	CN	H	CN	66	137
			Et	CO_2Me	Me	CO_2Me	37	137
H	$-(CH_2)_4-$		Me	H	H	CO_2Me	58	136
			Et	H	H	CN	68	137
Me	H	Me	Me	H	H	CO_2Me	53	136
Me	Et	H	Et	H	H	CN	53	137
Me	*n*-Pr	H	Me	H	H	CO_2Me	30	136
Me	*t*-Bu	H	Et	H	H	CN	10	137
Me	Me	Me	Me	H	H	CO_2Me	32	136
			Et	H	H	CN	60	137

TABLE 16. Coupling Products 49 from Olefins 45 (R^2 = H) and 48 and Alcohols 46[135]

olefin 45		alcohol 46	olefin 48	product 49
R^1	R^3	R^4	X	yield, %
Ph	H	Me	CN	50
$PhCH_2$	H	Me	CN	51
		Me	CO_2Me	39
$-(CH_2)_4-$		Me	CO_2Me	60
		H	CN	59
$CH_2{=}CH(CH_2)_2$	H	H	CO_2Me	40
$PhCH_2$	H	H	CO_2Me	57
n-Bu	H	H	CO_2Me	48

SCHEME 44[138]



1,2-adducts, which are coupled in situ with electron-poor olefins 51, yielding products 52 (Scheme 45 and Table 17).[139]

In the field of carbohydrates the tandem mercuration–radical coupling has been used in the synthesis of branched sugars, starting from the corresponding unsaturated glycals 53 and 55 and employing the electrophilic olefin 26 (Scheme 46 and Table 18).[140]

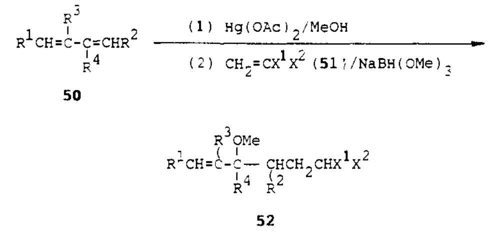
The solvomercuration–reductive coupling tandem process can be used to prepare lactones 58 and 60 starting from terminal olefins 57, either by employing Triton X-100 as a surfactant (Scheme 47)[135] or by previous isolation of the coupling products 59 (Scheme 48)[141] (Table 19).

In the prior case, depending on the reaction conditions in the hydrolysis step, the corresponding γ- or δ-lactones (60 or 58) can mainly be obtained (Scheme 48). Another possibility for obtaining lactones consists in carrying out the hydroxymercuration of the starting

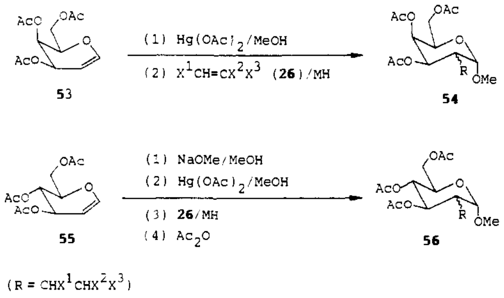
TABLE 17. Coupling Products 52 from Dienes 50, Olefins 51, and Methanol[139]

diene 50				olefin 51		product 52
R^1	R^2	R^3	R^4	X^1	X^2	yield, %
H	H	H	H	H	CN	47
				H	CO_2Me	34
				H	COMe	22
				Me	CN	24
				Cl	CN	60
Me	H	H	H	Cl	CN	59
H	H	Me	Me	Cl	CN	24
$-(CH_2)_2-$		H	H	Cl	CN	27

SCHEME 45[139]



SCHEME 46[140]



SCHEME 47[135]

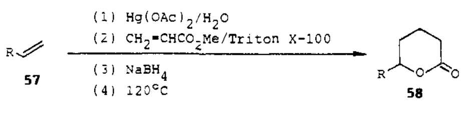


TABLE 18. Branched Sugars 54 and 56 from Glycals 53 and 55 and Olefins 26[140]

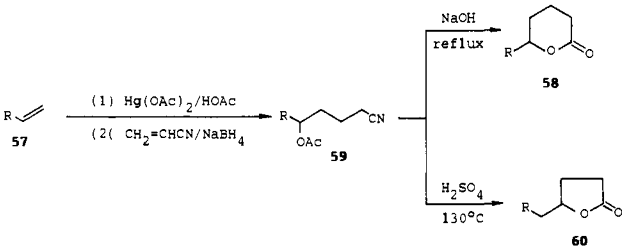
glycal	olefin 26 X^1	X^2	X^3	MH	product 54 or 56 yield, %	stereoselectivity R_{eq}/R_{ax}
53	H	H	CN	n-Bu_4NBH_4	60	67/33
	H	H	CN	n-Bu_3SnH	67	67/33
	H	H	CO_2Me	n-Bu_3SnH	55	71/29
	CN	H	CN	n-Bu_3SnH	55	90/10
	CO_2Me	H	CO_2Me	n-Bu_4NBH_4	50	>97/<3
	Me	CN	CN	n-Bu_3SnH	40	>95/<5
55	H	H	CN	n-Bu_3SnH	72	67/33
	CN	H	CN	n-Bu_3SnH	40	>95/<5

TABLE 19 Lactones 58 and 60 from Olefins 57 and Methyl Acrylate or Acrylonitrile[135,141]

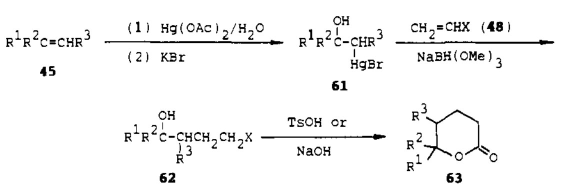
olefin 57 R	coupling product 59 yield,[a] %	γ-lactone 60 yield,[b] %	δ-lactone 58 yield, %	ref
Me	52	62	82[b]	141
n-Pr	50	63	80[b]	141
n-Bu			48[a]	135
n-C_5H_{11}	45	61	99[b]	141
$PhCH_2$			57[a]	135
n-$C_{11}H_{23}$[c]	40[c]		96[b]	141

[a] Based on the starting olefin 57. [b] Based on the coupling product 59. [c] Acetic acid was used in the mercuration step.

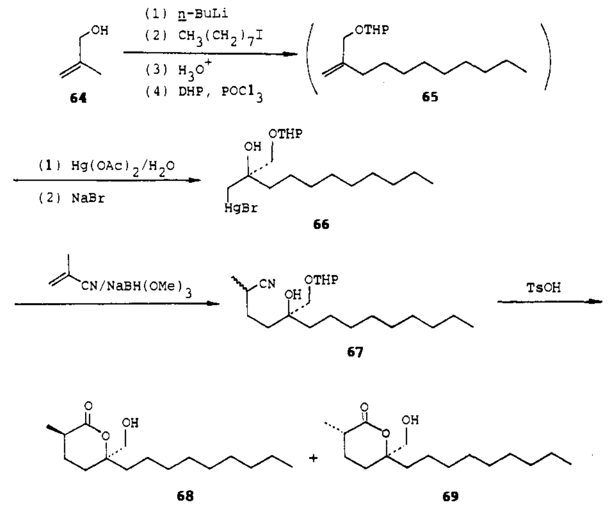
SCHEME 48[141]



SCHEME 49[142]



SCHEME 50[142]



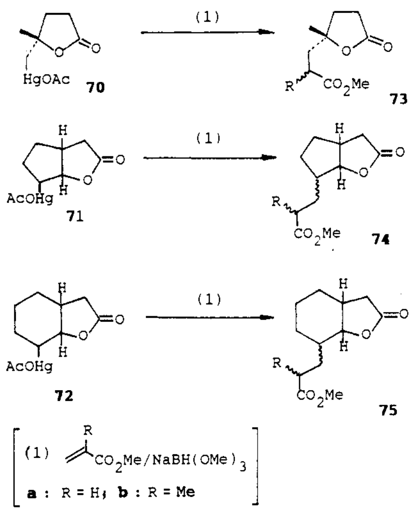
olefin 45 followed by the coupling reaction of the isolated mercurial 61 with the electrophilic alkene 48 and final cyclization of product 62, to give the corresponding lactone 63 (Scheme 49 and Table 20).[142]

TABLE 20. Lactones 63 from Olefins 45 and 48[142]

olefin 45 R^1	R^2	R^3	olefin 48 X	coupling product 62 yield,[a] %	lactone 63 yield,[b] %
H	H	Ph	CO_2Me	37	100
			CN	72	65
H	H	n-C_6H_{13}	CO_2Me	50	70
			CN	60	50
H	H	CH_2OCH_2Ph	CO_2Me	50	65
			CN	94	60
H	$-(CH_2)_4-$		CO_2Me	78	95
			CN	74	62
Me	Me	Et	CO_2Me	43	88

[a] Based on the organomercurial 61. [b] Based on the coupling product 62.

SCHEME 51[143]



This last strategy has successfully been used in the synthesis of the antibiotic (±)-malingolide 68,[142] as shown in Scheme 50. Thus, starting from the allylic alcohol 64 and through the not isolated intermediate 65, the corresponding hydroxymercuration is carried out, yielding the mercurial 66 (45% overall yield), which is coupled with methacrylonitrile to afford a 1:1 mixture of diastereoisomers 67 (49% yield); the final cyclization leads to the expected 1:1 mixture of the wanted antibiotic 68 and its diastereoisomer 69, which is easily separated by chromatography.

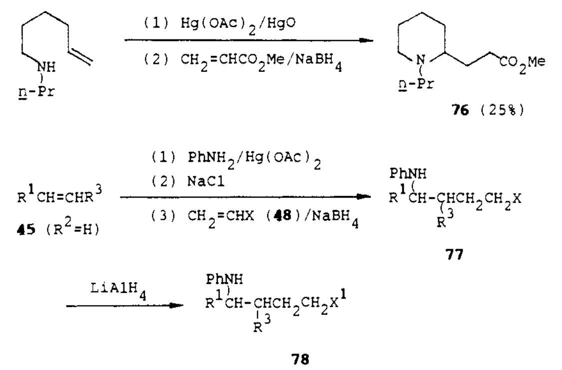
However, in the case of the mercurated lactones 70–72, the coupling reaction gives poorer yields in products 73–75 than when the corresponding iodine or selenium derivatives are used (Scheme 51 and Table 21).[143]

(ii) β-Nitrogenated Radicals. The tandem aminomercuration–reductive coupling has been studied far less than the corresponding oxymercuration process. Thus, the intra-[138] or intermolecular[144] amino-

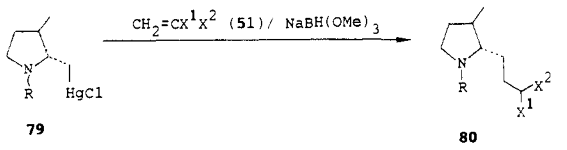
TABLE 21. Coupling Products 73–75 from Organomercurials 70–72[143]

organomercurial no.	electrophilic olefin R	coupling product no.	coupling product yield, %
70	H	**73a**	6
	Me	**73b**	18
71	H	**74a**	20
	Me	**74b**	18
72	H	**75a**	0
	Me	**75b**	0

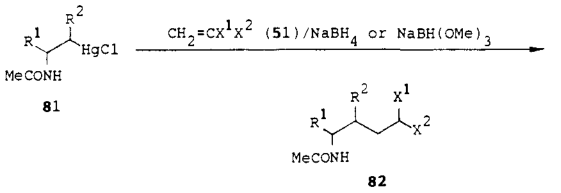
SCHEME 52[138,144]



SCHEME 53[145]



SCHEME 54[145,147,148]



mercuration is used in the first step in the generation of the amino mercurial intermediate, which is coupled in situ with an electrophilic olefin, yielding the corresponding products **76** or **77**; further reduction of the products **77** is an interesting method for the synthesis of amino alcohols or diamines **78** (Scheme 52 and Table 22).[144]

The above-described reaction can alternatively be carried out by isolating the starting amino mercurials; the coupling process with compounds **79** and electron-poor olefins **51** is shown in Scheme 53 and leads to the expected products **80** (Table 23).[145]

The coupling reaction fails when carried out starting from β-nitro or β-azido mercurials.[145] However, the use of β-amido mercurials, either isolated or generated in situ, leads to the expected products. Thus, the reaction of β-acetamidomercury compounds (obtained by acetamidomercuration of olefins with acetonitrile and mercury nitrate[146]) with electrophilic olefins **51** in the presence of a sodium borohydride leads to the coupling products **82** (Scheme 54 and Table 24).[145,147,148]

In the case of the coupling products **83** derived from acrylonitrile, the corresponding systems have been used for the preparation of pyrrolidines **84** (Scheme 55).[147]

TABLE 22. Functionalized Amines 77 and 78 from Olefins 45 (R^2 = H) and 48[144]

olefin 45 R^1	olefin 45 R^3	olefin 48 X	product 77 yield,^{a} %	product 78 X^1	product 78 yield,^{a} %
H	n-Bu	CN	39	CH_2NH_2	91
		CO_2Et	31	CH_2OH	85
H	Ph	CN	38	CH_2NH_2	85
		CO_2Et	31	CH_2OH	80
H	$PhCH_2$	CN	36	CH_2NH_2	86
		CO_2Et	30	CH_2OH	80
$-(CH_2)_3-$		CN	44^b	CH_2NH_2	89
		CO_2Et	35^b	CH_2OH	86
$-(CH_2)_4-$		CN	13 (47^b)	CH_2NH_2	87
		CO_2Et	39^b	CH_2OH	85

^{a}Based on the starting olefin **45**. ^{b}Triton X-100 is used as a phase-transfer catalyst.

TABLE 23. Substituted Pyrrolidines 80 from Amino Mercurials 79 and Olefins 51[145]

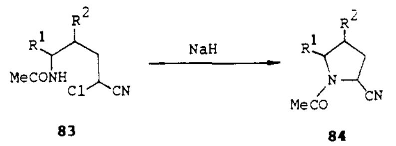
amino mercurial R	olefin 51 X^1	olefin 51 X^2	product 80 yield, %
$PhCH_2$	Cl	Cl	43
	Cl	CN	26
4-$MeOC_6H_4$	Cl	Cl	18
	Cl	CN	45

TABLE 24. Coupling Products 82 from Amidomercury Compounds 81 and Olefins 51[145,147,148]

amido mercurial 81 R^1	amido mercurial 81 R^2	olefin 51 X^1	olefin 51 X^2	product 82 yield, %	ref
H	Ph	H	CN	67	145
		H	CO_2Me	22	145
H	n-C_6H_{13}	H	CN	67	145
		H	CO_2Me	40	145
$-(CH_2)_3-$		Cl	CN	44	147
$-(CH_2)_4-$		H	CN	78	145
		H	CO_2Me	15	145
		Cl	CN	49	147, 148
Me	Me	H	CN	74	145
		H	CO_2Me	26	145
Et	Et	Cl	CN	a	147

^{a}Not reported.

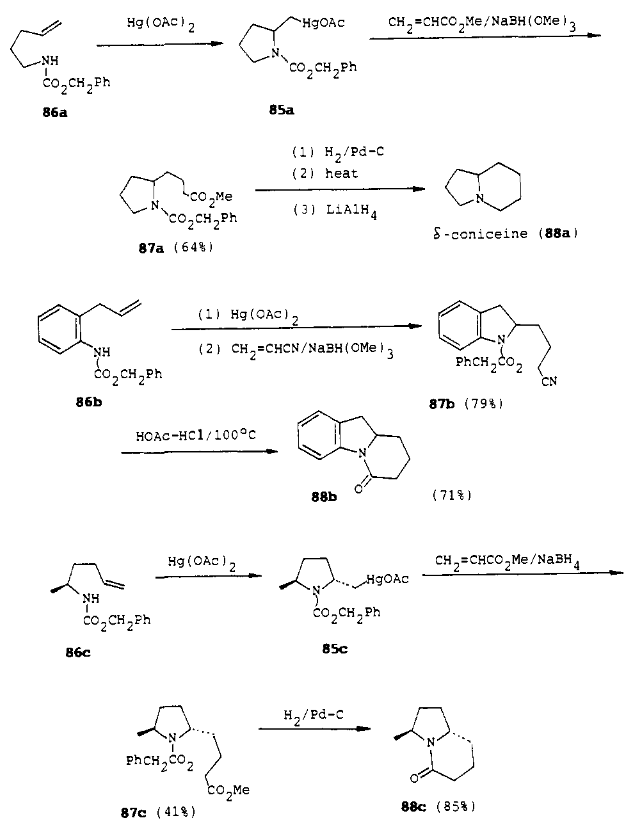
SCHEME 55[147]



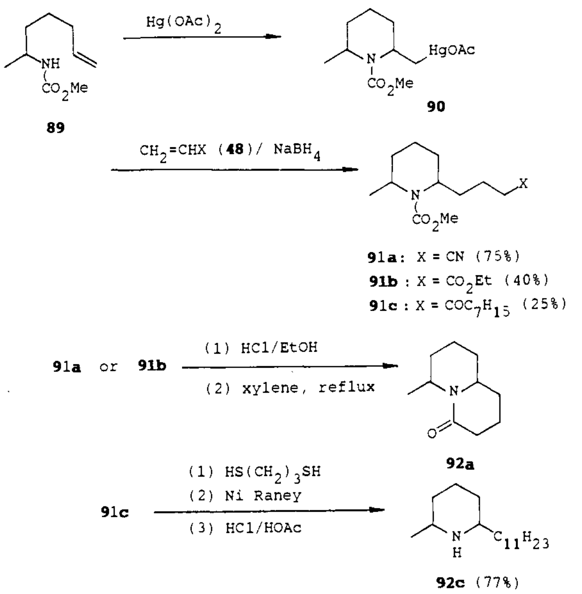
Other amidomercury compounds used in coupling processes are mercurated urethanes like **85** prepared by intramolecular amidomercuration[149] of unsaturated urethanes **86**; the corresponding coupling reaction with acrylic derivatives leads to the products **87**, which are adequate precursors for nitrogen-containing heterocycles **88**. The tandem amidomercuration–coupling can be carried out in situ, as is shown in the case of **87b** (Scheme 56).[150]

The process described above has successfully been applied to the synthesis of piperidinic systems **91** starting from the corresponding unsaturated urethanes **89** via a tandem mercuration–reductive coupling, the mercurial **90** being the intermediate. The resulting products are also adequate precursors for alkaloid type molecules like **92** (Scheme 57).[151]

SCHEME 56[150]



SCHEME 57[151]



SCHEME 58[162]

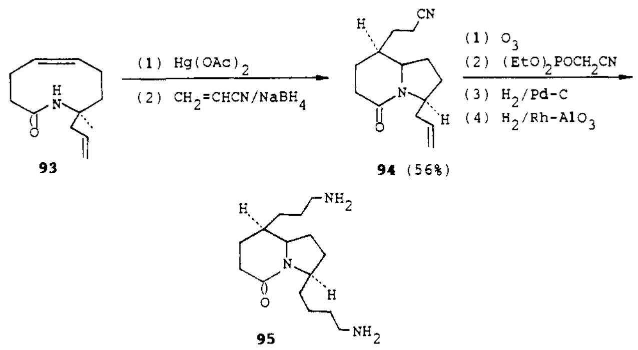


TABLE 25. Coupling Products 97 from Olefins 45 (R^2 = H) and 48 and Amides 96[155]

olefin 45		amide 96	olefin 48	product 97
R^1	R^3	R^4	X	yield, %
H	H	MeO	CN	32[a]
Me	H	Me	CN	30
		MeO	CN	68
n-Bu	H	Me	CN	77
		Me	CO_2Me	50
		MeO	CN	71
		MeO	COMe	40[a]
		MeO	CO_2Me	61[a]
$-(CH_2)_4-$		H	CN	40
		Me	CN	44
		MeO	CN	63
		NH_2	CN	57

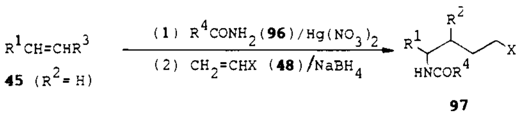
[a] A mixture of $Hg(NO_3)_2$ and HgO (2:1) was used in the mercuration step.

TABLE 26. Coupling Products 100 from Cyclopropanes 98, Olefins 26, and Methanol[156]

cyclopropanes 98		olefin 26			product 100
R^1	R^2	X^1	X^2	X^3	yield, %
H	Ph	H	H	CN	90
		H	H	CO_2Me	77
		H	H	Ph	38
		H	Me	CN	70
		H	Me	CO_2Me	67
		H	Cl	CN	87
		H	Cl	Cl	51
		CN	H	CN	90[a]
		CO_2Et	H	CO_2Et	95[a]
		CO_2Et	H	CO_2Et	42[b]
		Me	H	CN	21
		Me	H	CO_2Me	12
		CO_2Et	Me	CO_2Et	67
$-(CH_2)_4-$		H	H	CN	80
		H	H	CO_2Me	76
		H	H	Ph	34
		H	Me	CN	80
		H	Me	CO_2Me	68
		H	Cl	CN	76
		H	Cl	Cl	44
		CN	H	CN	84[a]
		CO_2Et	H	CO_2Et	80[a]
		CO_2Et	H	CO_2Et	35[b]
		Me	H	CN	22
		Me	H	CO_2Me	13
		CO_2Et	Me	CO_2Et	60

[a] The CN or CO_2Et groups are in a trans position. [b] The CN or CO_2Et groups are in a cis position.

SCHEME 59[155]



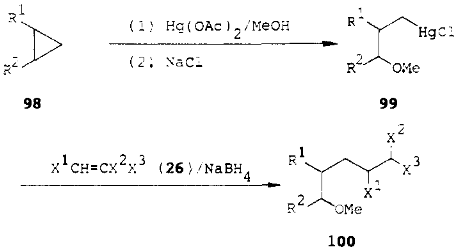
Recently, the in situ amidomercuration–coupling tandem reaction has been used in the key step of the preparation of the immunosuppressant tripeptide 95, starting from the lactams 93 via the intermediate 94 (Scheme 58).[152]

A general method for the addition of carboxamides, ureas, and urethanes 96 to unactivated olefins 45 consists in the use of mercury nitrate.[153,154] When this method is combined with the in situ reductive coupling reaction employing electrophilic olefins 48 as reagents, the corresponding products 97 are obtained (Scheme 59 and Table 25).[155]

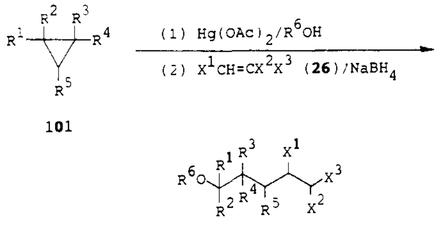
TABLE 27. Coupling Products 102 from Cyclopropanes 101, Olefins 26, and Methanol or Acetic Acid[157-159]

cyclopropane 101					solvent	olefin 26			product 102	
R^1	R^2	R^3	R^4	R^5	R^6	X^1	X^2	X^3	yield, %	ref.
H	$-(CH_2)_4-$		H	H	Me	H	H	CN	82	157, 158
					Me	H	H	CO_2Me	74	158
					Me	H	H	Ph	30	158
					Me	H	Me	CN	70	158
					Me	H	Me	CO_2Me	60	158
					Me	H	Cl	CN	84	158
					Me	H	Cl	Cl	38	158
					Me	CN	H	CN	87	158
					Me	CO_2Et	H	CO_2Et	70	158
					Me	CO_2Et	CO_2Et	H	33	158
					Me	Me	H	CN	18	158
					Me	Me	H	CO_2Me	11	158
					Me	CO_2Et	Me	CO_2Et	50	158
					Me	H	H	CN	87	157, 158
					Me	H	Me	CO_2Me	50	158
					Me	CO_2Et	H	CO_2Et	68	158
					Me	CO_2Et	Me	CO_2Et	74	158
n-C_6H_{13}	H	H	H	H	Me	H	H	CN	50	157, 158
					Me	H	Me	CO_2Me	33	158
					Me	CO_2Et	H	CO_2Et	55	158
					Me	CO_2Et	Me	CO_2Et	40	158
H	$-(CH_2)_4-$		H	H	Me	H	H	CN	82	158
					Me	H	Me	CO_2Me	60	158
					Me	CO_2Et	H	CO_2Et	70	158
					Me	CO_2Et	Me	CO_2Et	50	158
Et	Et	H	H	H	Me	H	H	CN	64	157, 158
Me	Me	Me	H	H	Me	H	H	CN	81	157, 158
					Me	H	Me	CO_2Me	50	158
					Me	CO_2Et	H	CO_2Et	71	158
					Me	CO_2Et	Me	CO_2Et	50	158
Me	H	Me	H	Me	Me	H	H	CN	20	157, 158
Me	Me	Me	Me	H	Me	H	H	CN	56	157, 158
Ph	H	H	H	H	MeCO	H	H	CN	62	159
					MeCO	H	Me	CN	41	159
					MeCO	H	Cl	CN	65	159
					MeCO	CO_2Et	H	CO_2Et	80	159
					MeCO	CO_2Et	Me	CO_2Et	45	159
n-C_6H_{13}	H	H	H	H	MeCO	H	H	CN	40	159
					MeCO	CO_2Et	H	CO_2Et	40	159
H	$-(CH_2)_4-$		H	H	MeCO	H	H	CN	65	159
					MeCO	H	Me	CN	46	159
					MeCO	H	Cl	CN	81	159
					MeCO	CO_2Et	Me	CO_2Et	46	159
Me	Me	Me	H	H	MeCO	H	H	CN	45	159
					MeCO	CO_2Et	H	CO_2Et	41	159
Me	Me	Me	Me	H	MeCO	H	H	CN	40	159

SCHEME 60[166]



SCHEME 61[157-159]



(d) γ-Substituted Radicals. γ-Substituted organomercury compounds are easily prepared by oxymercuration of cyclopropanes **98**,[3] and their isolation is usually carried out as the corresponding chloromercury derivatives **99**. The reductive coupling of these systems with electron-poor olefins **26** leads to the expected coupling products **100** (Scheme 60 and Table 26).[156]

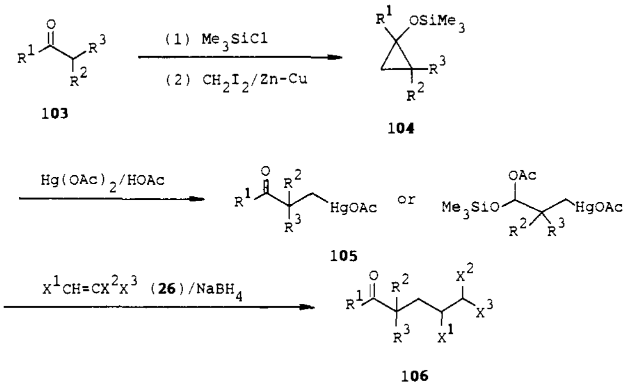
The process can be carried out in a one-pot manner without isolation of the organomercury intermediates. In this case the reaction has been studied for the methoxy-[157,158] and acetoxymercuration products.[159] Scheme 61 shows the mentioned reaction performed with the starting cyclopropanes **101**, in methanol or acetic acid as solvent, and an electrophilic olefin **26**, in which the expected coupling products **102** are isolated (Table 27).

Other γ-substituted organomercury compounds are the so-called homoenolates **105**, which are available from aldehydes or ketones **103** by successive silylation,[160] cyclopropanation,[161] and final mercuration of the isolated silylated cyclopropanols **104**.[162] When the organomercury compounds **105** are allowed to react in situ with an electrophilic olefin **26** and sodium borohydride,

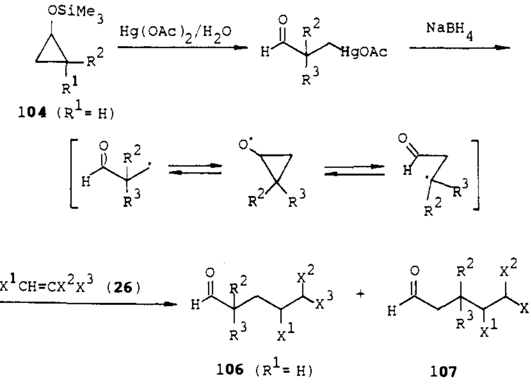
TABLE 28. Coupling Products 106 from Carbonyl Compounds 103 and Olefins 26[163,164]

carbonyl compound 103			olefin 26			product 106 yield, %	ref
R^1	R^2	R^3	X^1	X^2	X^3		
$-(CH_2)_4-$		H	H	H	CN	68	163
			H	H	COMe	64	163
			H	H	CO_2Me	62	163
			H	Me	CO_2Me	60	163
			CO_2Et	H	CO_2Et	58	163
			H	Cl	CN	50	163
			H	Me	CN	50	163
H	*n*-Bu	H	H	H	CN	60	164
			H	H	CO_2Me	52	164
			H	H	COMe	61	164
			H	Cl	CN	65	164
			H	Me	CN	40	164
			CO_2Et	H	CO_2Et	60	164
H	Me	Me	H	H	CN	51	164
			H	H	CO_2Et	49	164
			H	Cl	CN	51	164
			H	Me	CN	30	164
			CO_2Et	H	CO_2Et	45	164

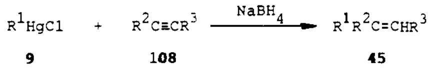
SCHEME 62[160-164]



SCHEME 63[164]



SCHEME 64[165]



$$\underset{9}{R^1HgCl} + \underset{108}{R^2C{\equiv}CR^3} \xrightarrow{NaBH_4} \underset{45}{R^1R^2C{=}CHR^3}$$

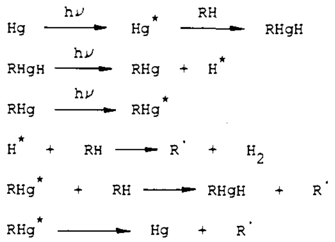
TABLE 29. Coupling Products 106 (R^1 = H) and 107 from Silylated Cyclopropanols 103 (R^1 = H) and Olefins 26[164]

cyclopropanol 103		olefin 26			product 106 + 107 yield, %
R^2	R^3	X^1	X^2	X^3	
n-Bu	H	H	H	CN	55
		H	H	CO_2Et	50
		H	Cl	CN	35
		CO_2Et	H	CO_2Et	36
Me	Me	H	H	CN	47
		H	H	CO_2Et	45
		H	Cl	CN	45
		CO_2Et	H	CO_2Et	45

TABLE 30. Coupling Products 45 from Organomercurials 9 and Alkynes 108

mercurial 9	alkyne 108		product 45	
R^1	R^2	R^3	yield, %	*E*/*Z* ratio
c-C_6H_{11}	H	Ph	8	30/70
t-Bu	H	Ph	10	7/93
n-C_6H_{13}	H	CO_2Me	10	69/31
c-C_6H_{11}	H	CO_2Me	35	56/44
t-Bu	H	CO_2Me	41	28/72
c-C_6H_{11}	CO_2Me	CO_2Me	21	36/64
t-Bu	CO_2Me	CO_2Me	54	58/42

SCHEME 65[166]



$$Hg \xrightarrow{h\nu} Hg^* \xrightarrow{RH} RHgH$$
$$RHgH \xrightarrow{h\nu} RHg + H^*$$
$$RHg \xrightarrow{h\nu} RHg^*$$
$$H^* + RH \longrightarrow R^\cdot + H_2$$
$$RHg^* + RH \longrightarrow RHgH + R^\cdot$$
$$RHg^* \longrightarrow Hg + R^\cdot$$

the corresponding coupling products 106 are obtained (Scheme 62 and Table 28).[163,164]

In the case of the aldehyde derivatives (103 with R^1 = H), described in Scheme 62, it is necessary to treat the reaction product with potassium fluoride at the end of the reaction in order to get the final desilylation.

An alternative to the reaction described above for aldehyde derivatives consists in the hydroxymercuration of the corresponding silylated cyclopropanols (104 with R^1 = H) before the second reaction step. In this case a mixture of reaction products 106 and 107 is obtained, which arises from the corresponding equilibration of the radical intermediates (Scheme 63 and Table 29).[164]

3. Reaction with Acetylenes

The reaction of radicals generated by the "mercury method" with acetylenes has been the subject of a sole publication.[165] When different primary, secondary, or tertiary organomercury compounds 9 are treated with several alkynes 108 in the presence of sodium borohydride, a *Z*/*E* mixture of the corresponding coupling products 45 is obtained (Scheme 64 and Table 30).

TABLE 31. Products from the Mercury-Photosensitized Decomposition of Sulfur-Containing Compounds[167,168]

starting material	product ratio, %							
	EtH	Me_2S_2	MeSH	MeH	MeS_3Me	Me_2S	H_2S	H_2
Me_2S	40.6	28.8	11.8	3.0				
Me_2S_2	13.4	26.5	22.0	1.9	25.9			
MeSH	17.5	13.1		6.6		13.8	38.5	13.6

SCHEME 66[167]

$$Hg \xrightarrow{h\nu} Hg^* \xrightarrow{Me_2S} Me_2S^* + Hg$$

$$Me_2S^* \longrightarrow MeS^\cdot + Me^\cdot$$

$$2\ MeS^\cdot \longrightarrow MeSSMe$$

$$2\ MeS^\cdot \longrightarrow MeSH + (H_2CS)$$

$$2\ Me^\cdot \longrightarrow EtH$$

$$Me^\cdot + MeS^\cdot \longrightarrow MeH + (H_2CS)$$

SCHEME 67[169-171]

$$1^{st}\ \text{wave:} \quad RHgX + e \rightleftharpoons RHg^\cdot + X^-$$

$$(RHg^\cdot \longrightarrow 1/2\ R_2Hg + 1/2\ Hg)$$

$$2^{nd}\ \text{wave:} \quad RHg^\cdot + e \longrightarrow R^- + Hg$$

$$R^- + HX \longrightarrow RH + X^-$$

The relative reaction rate of the intermediate radical with alkenes and alkynes was studied, concluding that the last reagents react 3.0–5.2 times more slowly than the alkenes. These results contrast with the addition of nucleophiles to both unsaturated systems.

IV. Radicals Generated by Other Methods

A. Radicals Generated by Excited Mercury

Although of no synthetic interest, the reaction of photosensitized mercury with 3-methylpentane glass at 5–77 K leads to radicals, through the corresponding alkylmercury hydride species (Scheme 65).[166]

Likewise, the reaction of photosensitized mercury with different sulfur-containing compounds such as dimethyl sulfide,[167] dimethyl disulfide,[167] and methyl or ethyl mercaptan[168] has been studied by mass spectrometry (Table 31). Scheme 66 shows the proposed mechanism for the case of dimethyl sulfide.[167]

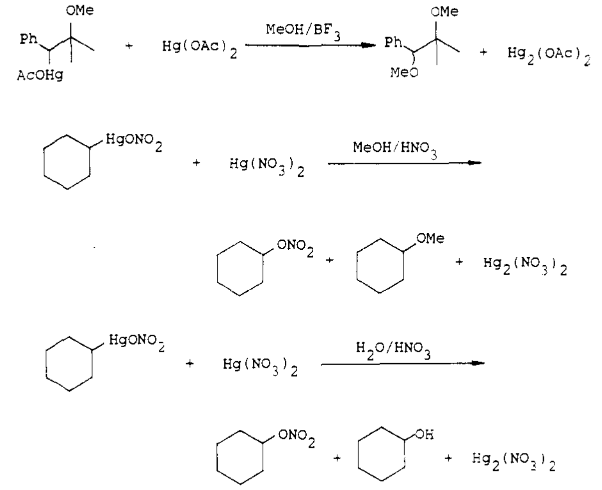
B. Electrochemically Generated Radicals

Depending on the reaction conditions, the formation of a mixture of products has been observed in the electrochemical reduction of organomercury compounds. This process can easily be explained by considering the existence of an alkyl- or arylmercury radical intermediate. This species would be generated in the first phase of the process (first polarographic wave), and a second step (second polarographic wave) would give the reduction products. In an alternative way, the generated radical can suffer disproportionation to afford symmetrization products. However, in these processes the corresponding dimer has never been observed (Scheme 67).[169-171]

C. Radicals Generated by Autoxidation

The oxidation of organomercury compounds by means of mercury(II) salts, the so-called "autoxidation", constitutes a method of interest for the substitution of a mercury atom by a nucleophile (Scheme 68).[172]

SCHEME 68[172]



SCHEME 69[172]

$$HgX_2 \rightleftharpoons X^\cdot + XHg^\cdot$$

$$HgX_2 + ROH \rightleftharpoons ROHgX + HX$$

$$ROHgX \rightleftharpoons RO^\cdot + XHg^\cdot$$

$$R'HgX \rightleftharpoons R'^\cdot + XHg^\cdot$$

$$XHg^\cdot + ROHgX \longrightarrow RO^\cdot + Hg_2X_2$$

$$RO^\cdot + R'HgX \longrightarrow R'OR + XHg^\cdot$$

$$XHg^\cdot + HgX_2 \longrightarrow X^\cdot + Hg_2X_2$$

$$X^\cdot + R'HgX \longrightarrow R'X + XHg^\cdot$$

$$2\ XHg^\cdot \longrightarrow Hg_2X_2$$

The proposed mechanism for this process is of a radical type, this conclusion being based on the fact that the reaction is inhibited by means of oxygen and is capable of polymerizing acrylonitrile (Scheme 69).[172]

D. Radicals Generated by Means of Metallic Salts

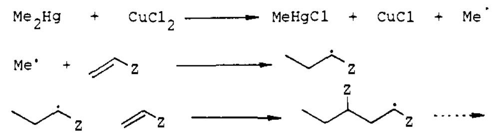
More general than the case of the "autoxidation" (section C) is the use of other metallic salts for the generation of radicals starting from dialkylmercury compounds, for instance, iridium(IV) salts; the obtained radicals have been the object of broad theoretical, spectroscopic, and chemical study.[173,174] The proposed mechanism is shown in Scheme 70: as can be seen, in the first step a charge transfer between the iridium salt and the organomercury compound is generated. Recently, the existence of stable complexes of this type has been demonstrated, such as the complex prepared from the 1:1 complex mercury(II) trifluoroacetate–EDTA and hexamethylbenzene; its structure has been analyzed by X-ray diffraction.[175]

On the other hand, organomercury compounds have been used as initiators or accelerators in radical polim-

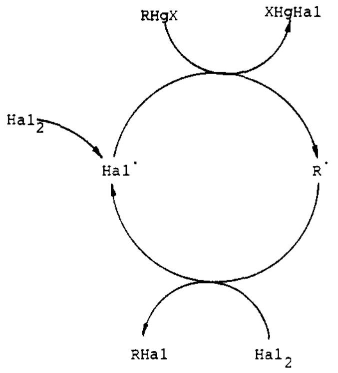
SCHEME 70[173]

$$R_2Hg + IrCl_6^{2-} \longrightarrow R_2Hg^{+\cdot} + IrCl_6^{3-}$$
$$R_2Hg^{+\cdot} \longrightarrow RHg^+ + R^\cdot$$
$$R^\cdot + IrCl_6^{2-} \longrightarrow R^+ + IrCl_6^{3-}$$
$$R^+ + Cl^- \longrightarrow R(-H) + RCl$$

SCHEME 71[178]



SCHEME 72[180,181]



erizations of olefins[176–178] and dienes,[179] such as styrene,[176] methyl acrylate,[176–178] vinyl acetate,[176] acrylonitrile,[178] or butadiene.[179] For instance, the corresponding process using copper(II) chloride as a reagent for the generation of the initiator, in this case, the methyl radical from dimethylmercury, is shown in Scheme 71.[178]

E. Radicals Generated by Halodemercuration

Radical intermediates have been proposed in reactions of organomercury compounds, bearing the metal atom on an sp^3-hybridized carbon atom, with bromine[180,181] or iodine,[182] based on stereochemical data. The reaction products are in all cases the corresponding alkyl halides (Scheme 72). In polar solvents, a competing nonradical halodemercuration can occur.[183]

However, when the organomercury compound bears the metal atom on an sp^2-hybridized carbon atom, the corresponding halodemercuration gives different stereochemical results depending on the solvent used. For instance, in the bromodemercuration in pyridine, a retention in the configuration is observed, whereas in carbon disulfide the main process occurs with inversion. Taking these facts into account, a radical mechanism does not seem to be general for the mentioned process.[184]

V. Conclusions

From the chemistry described in this survey it can be conclused that one of the most important applications of organomercury compounds in organic synthesis is related to their potential for generating radical intermediates. The most general method for carrying out this generation, which can also be performed thermally, photochemically, or by other methods, is the so-called "mercury method" by means of sodium borohydride. Primary, secondary, and tertiary unfunctionalized or α-, β-, and γ-functionalized radicals bearing an oxygenated or nitrogenated functional group have been obtained by this methodology. The further reaction of the generated radicals with different unsaturated systems through an intra- or intermolecular reaction constitutes an efficient procedure of obtaining regiospecific but not stereospecific carbon–carbon bonds and represents an adequate way to construct organic molecules.

VI. References

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