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Review

Stereo- and Regio-selective Halogenation and Pseudohalogenation via Organometallc Compounds*

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Synthetically useful methods for the stereo- and regio-selective preparation of organic halides and pseudohalides *via* organometallic compounds are reviewed from synthetic viewpoint. Such metals as boron, thallium, silicon and mercury have proved to be of great importance for the purpose. Halogeno- and pseudohalogeno-demetallation at *ipso* position is generally involved in the cases of alkyl-, aryl- and alkynyl-organometallic compounds, while in the alkenyl case the reaction can be normally best explained by addition-elimination mechanism. Preferred halogenolysis and pseudohalogenolysis reagents are molecular halogens, mixed halogens, N-halogenosuccinimides, and copper (II) and (I) halides and pseudohalides.

KEY WORDS: Halogenodemetallation/ Pseudohalogenodemetallation/ Organoboranes/ Organothallium Compounds/ Organosilanes/ Organomercurials/

Conversion of the carbon-metal bond of organometallic compounds into carbon-halogen bond and carbon-pseudohalogen bond is generally a well-known process (halogenodemetallation and pseudohalogenodemetallation) which may be useful for the preparation of organic halides and pseudohalides. In some case there appear to be few synthetic advantages to be gained by employing organometallic compounds as intermediates in the synthesis of organic halides for the following reasons: the starting metarials for the preparation of organometallics are sometimes either (1) organic halides themselves, (2) compounds derived from organic halides (organomagnesium or -lithium compounds), or (3) compounds readily halogenated directly (arenes, diazonium salts *etc*). Nevertheless, a combination of this process with highly stereo- and regio-selective direct metallation producing specific organometallic compounds makes selective halogenation and pseudohalogenation of organic compounds possible which are not easily accessible by direct halogenation method. Out of many organometallic compounds so far employed, those using such metals as boron, thallium, silicon, and mercury seem to be especially important for this purpose. Preferred halogenolysis reagents are generally molecular halogens, mixed halogens, N-halogenosuccinimides, and copper (II) and (I) halides and pseudohalides. We would like to describe here representative examples of such reactions from synthetic viewpoint.

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* This review article was accepted on the occasion of the retirement of Professor Emeritus Yuzo Inouye and is dedicated to him.

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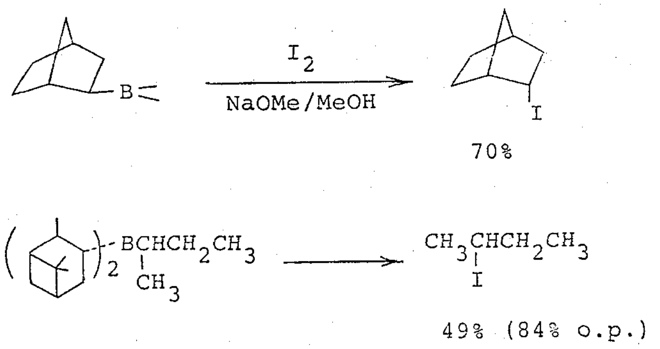
Boron Alkylboranes are easily accessible compounds by hydroboration of olefins. Although alkylboranes are relatively inert to iodine, an iodonolysis reaction (iododeboronation) occurs rather smoothly under basic conditions *via* alkylborates.[1,2] This is a convenient procedure for the conversion of terminal olefins into primary alkyl iodides (Scheme 1). The reaction proceeds generally with inversion of configuration of the carbon-carbon bond and this is an effective route to optically active alkyl iodides as shown in Scheme 2.[3]

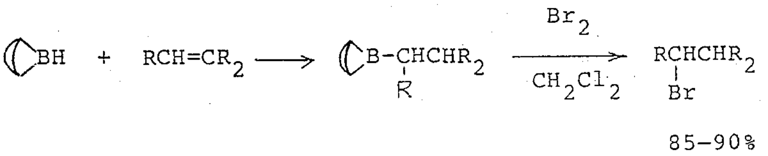
$$R'CH = CH_2 \xrightarrow[HB\langle]{} R_3B \xrightarrow[NaOMe/MeOH]{I_2} [R_3\bar{B}OMe] \longrightarrow \underset{84\text{–}95\%}{RI} \qquad (1)$$



(2)

Alkylboranes similarly react with bromine to give the corresponding alkyl bromides with inversion of configuration (Scheme 3).[4,5] This reaction can be applied especially well to the preparation of primary alkyl bromides. On the contrary, a bromonolysis reaction (bromodeboronation) under acidic or neutral conditions proceeds *via* a free-radical chain mechanism to give the expected alkyl bromides in over 80% yield, the secondary alkylboranes being more reactive than the primary ones.[6] The use of B-sec-alkyl-9-borabicyclo[3.3.1]nonanes is especially efficient for this convenient procedure of the anti-Markovnikov hydrobromination of internal olefins (Scheme 4).[7]

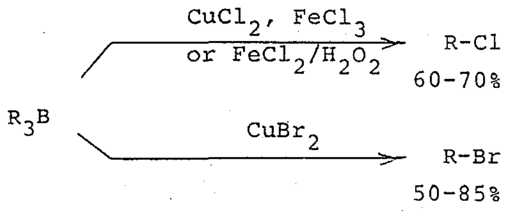
$$RCH = CH_2 \xrightarrow[THF]{BH_3} (RCH_2CH_2)_3B \xrightarrow[NaOMe/MeOH]{Br_2} \underset{65\text{–}99\%}{RCH_2CH_2Br} \qquad (3)$$



(4)

Alkylboranes can be converted to alkyl chlorides by using several reagents in which copper (II) chloride[8,9] and iron (III) chloride[9] seem to be most convenient

(Scheme 5). Copper (II) bromide also works as a bromonolysis reagent.[8,9]



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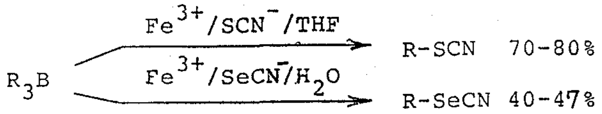
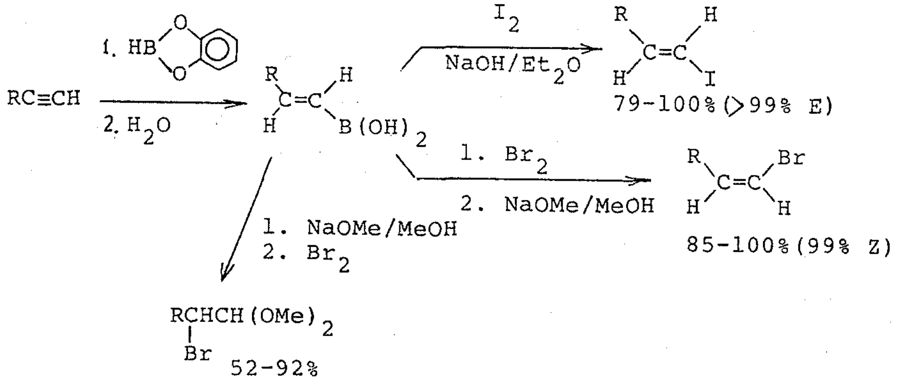
The carbon-boron bond of alkylboranes can be converted to the carbon-thiocyanato bond and carbon-selenocyanato bond by the reaction with iron (III) salt and potassium thiocyanate and selenocyanate, respectively (Scheme 6).[9,10]



(6)

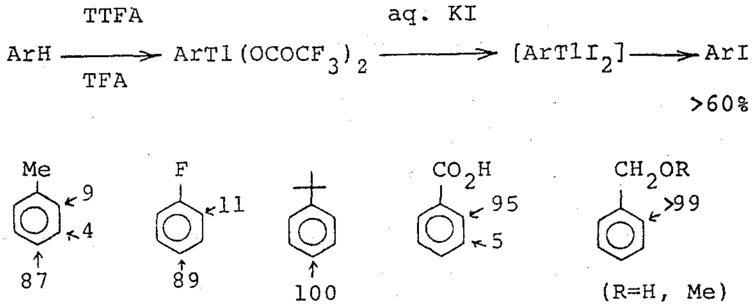
Alkenyl-, aryl-, and alkynylboranes behave a completely different way to iodine and bromine, and the general reaction is a highly unique carbon-carbon bond formation. On the other hand, in the case of alkenylboronic acids, readily prepared *via* the hydroboration of 1-alkynes with catecholborane followed by hydrolysis, the corresponding alkenyl halides can be prepared in high yields by treatment with iodine and bromine under basic conditions (Scheme 7).[11] The addition-elimination



(7)

mechanism was proposed for explaining the stereochemical result; *trans* addition of I^+ and OH^- followed by *syn*-elimination of boron moiety and OH group for iodonolysis, *trans* addition of Br_2 followed by *anti*-elimination of boron moiety and bromine for bromonolysis. Interestingly, the addition of a basic methanol solution of alkenylboric acids to a methanol solution of bromine resulted in the one-stage synthesis of α-bromo acetals (Scheme 7).[12]

Thallium The C-Tl bond of various organothallium compounds can be readily converted to the C-X (X=halogen, pseudohalogen) bond by treatment with various reagents.[13] The characteristics of the reaction are found especially in the preparation of aryl halides and pseudohalides, because aromatic thallation with thallium (III) acetate (TTA) and trifluoroacetate (TTFA) gives good to excellent yields of arylthallium (III) compounds highly regiospecifically and halogeno- and pseudohalogenodethallation occurs at the position where Tl was previously attached (*ipso*-substitution). Synthetically most useful reaction seems to be a facile formation of aryl iodides which can be obtained spontaneously by treatment with KI, keeping all of the orientation controll potential inherent in the initial thallation process. Typical examples are shown in Scheme 8 where the average yields of aryl iodides are over 60% yields.[14–17] Aryl chlorides and bromides are obtained by reaction with copper (II) or (I) chloride and bromide respectively, 1,4-dioxane being the solvent of choice.[18] Treatment with KBr followed by thermolysis[19] and that with Br_2 in CCl_4[20] also give aryl bromides. Aryl fluorides can be obtained by treatment of arylthallium (III) compounds with KF followed by a gaseous BF_3 in cyclohexane.[21]



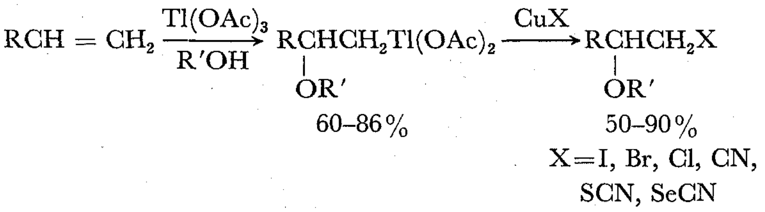
(8)

Aryl cyanides are prepared by treatment of these with copper (I) cyanide in MeCN[22] or by irradiation of an aqueous KCN solution of these.[23] Similarly, aryl thiocyanates can be produced in good yields by the reaction with copper (II) and potassium thiocyanates in dioxane[24] or photochemically with KSCN as above.[25] Aryl selenocyanates are prepared by treatment with copper (II) selenocyanate.[26] All these halogeno- and pseudohalogeno-dethallation are summarized in Scheme 9.

$$ArTl\,(OCOR)_2 \longrightarrow Ar\text{-}X \qquad (9)$$

aq. KI or I_2	>70% (X=I)
$CuBr_2$, KBr/Δ or Br_2	20–90% (X=Br)
$CuCl_2$ or Cu_2Cl_2	40–85% (X=Cl)
KF/BF_3	50–79% (X=F)
CuCN or KCN/hν	30–80% (X=CN)
$Cu(SCN)_2$ or KSCN/hν	35–80% (X=SCN)
$Cu(SeCN)_2$	78–94% (X=SeCN)

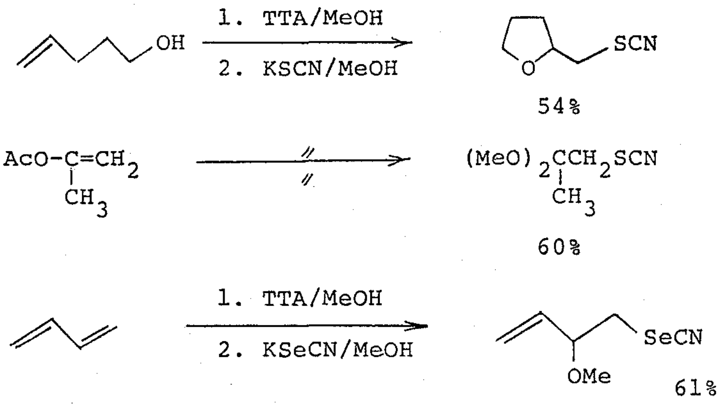
Treatment of organothallium compounds prepared by oxythallation of olefins with copper (I) iodide, bromide, and chloride in MeCN results in the replacement of the $Tl(OAc)_2$ moiety by the corresponding halogen (*ipso*-substitution) to give various kinds of β-substituted alkyl halides in good yields.[27] Similarly, the Tl moiety can be replaced by CN with copper (I) cyanide,[27] SCN with potassium



$$\mathrm{RCH=CH_2}\xrightarrow[\mathrm{R'OH}]{\mathrm{Tl(OAc)_3}}\underset{\substack{|\\ \mathrm{OR'}\\ 60\text{–}86\%}}{\mathrm{RCHCH_2Tl(OAc)_2}}\xrightarrow{\mathrm{CuX}}\underset{\substack{|\\ \mathrm{OR'}\\ 50\text{–}90\%\\ \mathrm{X=I,\ Br,\ Cl,\ CN,}\\ \mathrm{SCN,\ SeCN}}}{\mathrm{RCHCH_2X}}$$

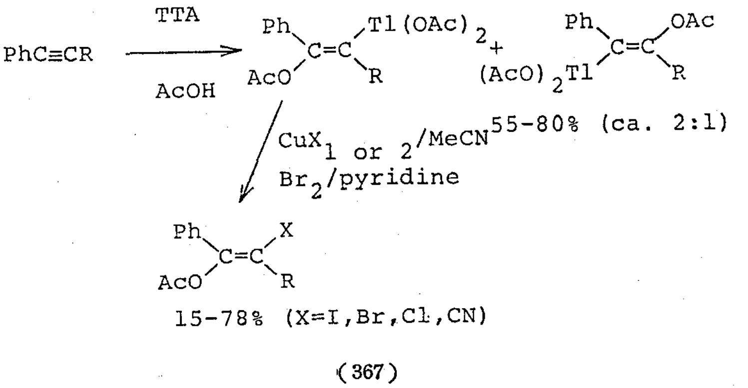
(10)

and/or copper (I) thiocyanate,[27,28] and SeCN with potassium selenocyanate (Scheme 10).[26] It should be worth to refer that thallium can be introduced regiospecifically to the terminal carbon in the case of 1-olefin. In the synthesis of alkyl thiocyanates and selenocyanates it is not necessary to isolate the intermediate oxythallation adducts and the *in situ* oxythallation of olefins followed by reaction with KSCN and KSeCN gives the products.[27,28] Typical examples are shown in Scheme 11.



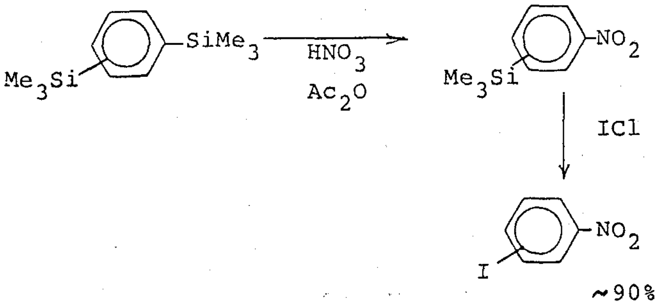
(11)

Acetoxythallation of alkylphenylacetylenes affords alkenylthallium (III) compounds (*trans*-addition), halogeno- and cyano-dethallation of which being conducted by reaction with the corresponding copper (II) or (I) salts in MeCN or with bromine in pyridine to give alkyl halides and pseudohalides stereospecifically (Scheme 12).[29] The method, however, is not synthetically useful, because the acetoxythallation step gives a *ca.* 2:1 mixture of regiospecific isomers. Acetoxymercuration of these acetylenes proceeds more regiospecifically as will be described later.



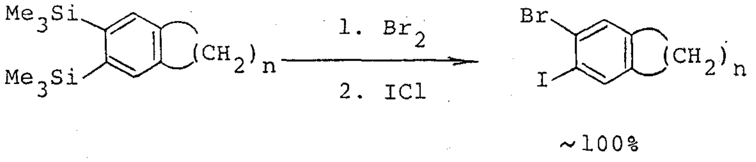
(12)

Silicon Although it has been known that the C-Si bond of aryltrimethylsilanes and tetraarylsilanes can be converted to the carbon-halogen bond by treatment with iodine[30] and bromine,[31,32] many such silanes have generally been prepared by *in situ* Grignard reactions or *via* aryllithium or -sodium derivatives, the starting compounds of which being the corresponding halides.[33] Therefore, the method does not seem to be so useful for preparation of aromatic halides, and yet there are several examples of regiospecific halogenation which may be worth to refer from synthetic viewpoint. For example, iodine monochloride has proved particularly effective for iododesilylation (*ipso*-substitution) and the reaction was successful even when the aromatic ring is substituted by strongly electron withdrawing groups; *o*-, *m*-, and *p*-iodonitrobenzenes have been prepared (Scheme 13).[34] *o*-, *m*-, and *p*-Bis(trimethylsilyl)benzenes have been converted to *o*-, *m*-, and *p*-diiodobenzenes respectively by treatment with ICl in over 90% yields.[35,36]



(13)

Sequential electrophilic desilylations of 4,5- and 3,4-bis-(trimethylsilyl)benzocyclobutenes, as well as 5,6-bis(trimethylsilyl)benzocyclopentene, by bromine followed by ICl, yielded the corresponding *ortho* bromoiodo aromatics (Scheme 14).[37,38] With 3,4-isomer, 4-bromo-3-iodo-benzocyclobutene was obtained (Scheme 15).[38] This regiospecificity results from the fact that halogenodesilylation occurs at the 4-position 500 times faster than at the 3-position.



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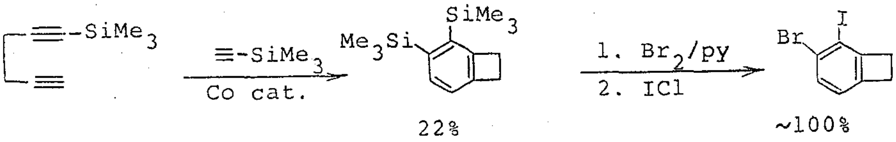
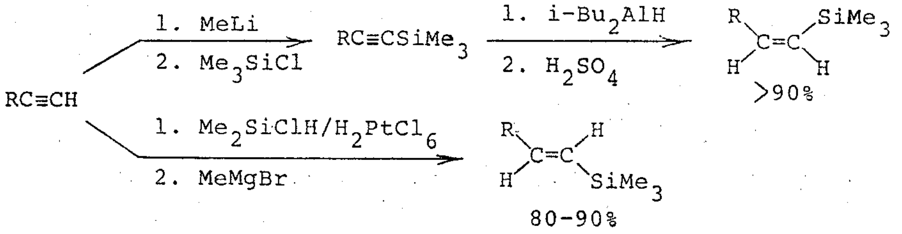


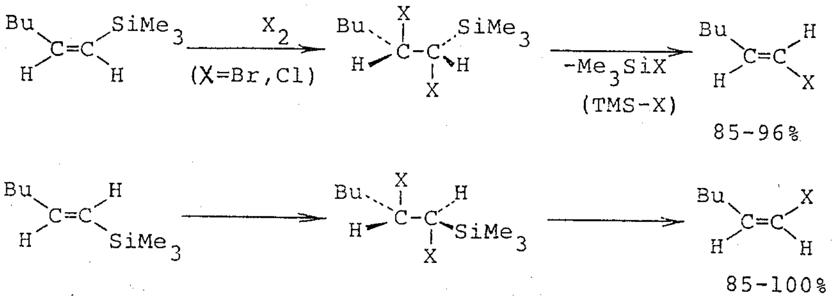
(15)

The C-Si bond of alkenylsilanes, prepared stereospecifically by several methods as shown in Scheme 16,[39,40] can be transformed to the C-halogen bond *via* stereospecific *trans*-addition–*trans*-elimination mechanism. For example, Z-1-trimethyl-



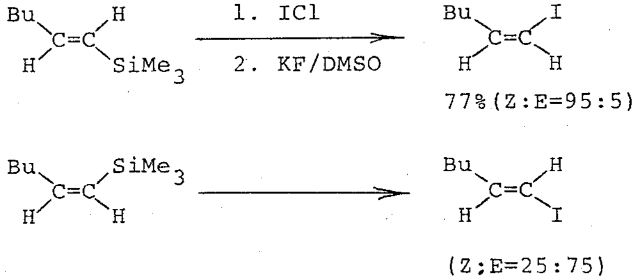
(16)

silylhexene reacts with either Cl_2 or Br_2 at −78°C to yield the respective *threo*-1-trimethylsilyl-1,2-dihalogenohexanes. These undergo *trans*-elimination of the elements of TMS-X on treatment with sodium methoxide in methanol or $KF \cdot 2H_2O$ in dimethyl sulfoxide to yield E-1-bromohexane or E-1-chlorohexene almost exclusively. Likewise, from E-isomer, Z-1-halogenohexene was produced (Scheme 17).[40]



(17)

The reaction of iodine with alkenyltrimethylsilanes followed by elimination of trimethylsilyl iodide to yield alkenyl iodides is more complex and the stereochemistry of the reaction and the product yield depend on the reaction conditions. However, iodine monochloride has proved more effective. Thus, E-1-trimethylsilylhexene reacts with ICl in CCl_4 at 0°C to give an adduct which loses trimethylsilyl chloride on treatment with KF in DMSO to yield almost pure Z-1-iodohexene, while Z-isomer affords predominantly E-1-iodohexene (Scheme 18).[41,42]

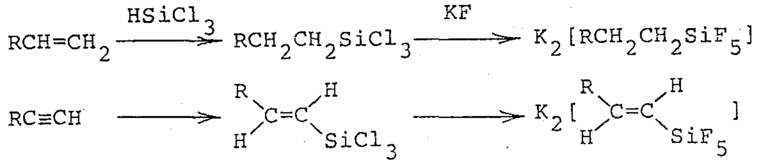


(18)

While the C-Si bond of alkyltrichlorosilanes is not easily cleaved by electrophiles, the C-Si bond of the corresponding dipotassium alkylpentafluorosilicates is cleaved to give alkyl halides and pseudohalides.[43] These silicates are easily prepared by reaction of alkyltrichlorosilanes with KF, and, unlike RLi or RMgBr, are air stable, crystalline solids which can be isolated by filtration. Facile halogenoand pseudohalogenodesilylation of these silicates makes the procedure synthetically very useful (Scheme 19).

$$\mathrm{RSiCl_3} \xrightarrow{\text{aq. KF}} \mathrm{K_2[RSiF_5]} \longrightarrow \mathrm{R\text{-}X} \qquad (19)$$

The well-established hydrosilylation of the unsaturated compounds with $HSiCl_3$ provides the most convenient route for organotrichlorosilanes with high regio- and stereo-selectivity in the presence of H_2PtCl_6 as catalyst (cf. Scheme 16).[44] In the case of linear alkenes, either terminal or internal, the terminal *anti*-Markovnikov adducts are produced exclusively. In the case of terminal alkynes, the addition of $HSiCl_3$ across the triple bond occurs in a *cis* fashion to give E-alkenyltrichlorosilanes (Scheme 20). Typical examples of the reaction of the silicates obtained from alkenes with halogens are shown in Scheme 21.[43] The reaction of alkylpentafluorosilicates with NBS(N-bromosuccinimide) to yield 1-bromoalkanes tolerates esters, as well as C-C double bonds (Scheme 22).[43] The silicates also undergo electrophilic cleavage by anhydrous copper (II) chloride or bromide to yield alkyl chlorides or bromides respectively in over 60% yield. Silicates of norbornyl system react with bromine or NBS in polar solvents to give 2-norbornyl bromides of inverted (at least 95%) stereochemistry (Scheme 23).[43]



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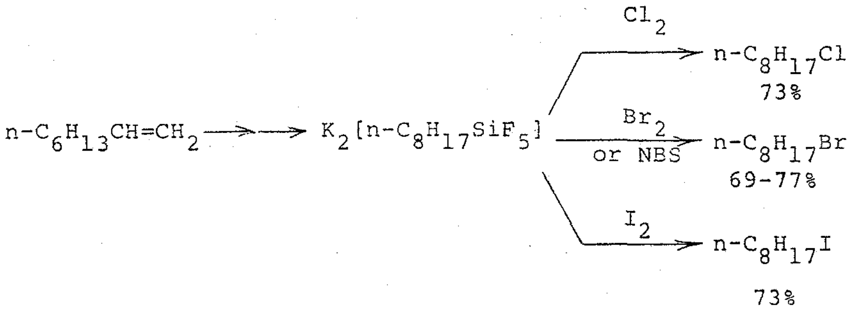

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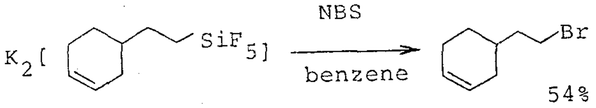
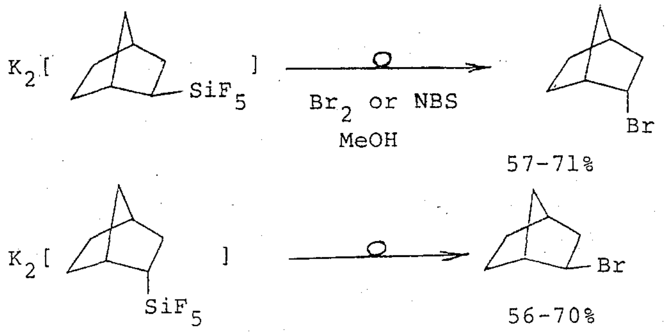


(22)

Alkenylpentafluorosilicates undergo electrophilic cleavage by NBS, $CuCl_2$ or $CuBr_2$ to yield the corresponding alkenyl bromides or chlorides with retention of stereochemistry. Similarly, they react with copper (II) thiocyanate to yield alkenyl thiocyanates with retention of configuration (Scheme 24).[45] The mechanism involving an alkenylcopper species is proposed in these cases.[43]



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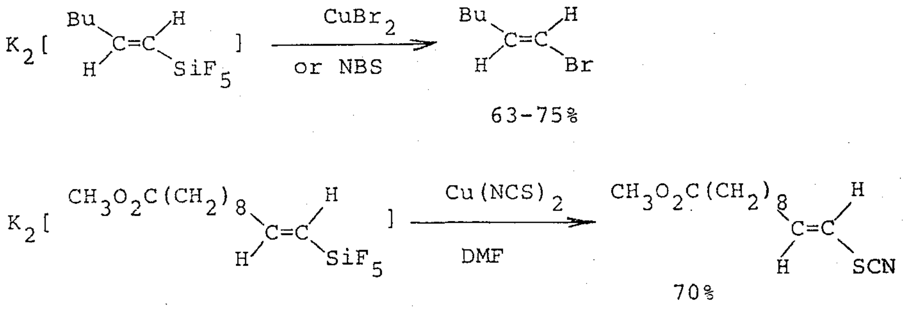
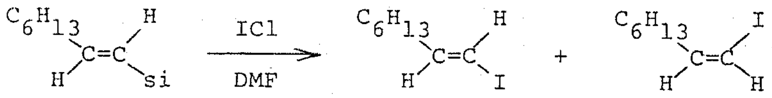


(24)

Stereochemistry in cleavage reactions of alkenylsilicon compounds with ICl depends upon the kind of silicon moiety and the nature of the solvent. The results of the reactions in DMF are shown in Scheme 25.[43]

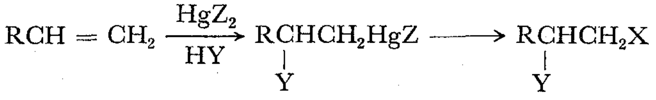


(25)

si=SiF_5^{2-}	57%	99 : 1
si=SiF_3	76%	95 : 5
si=$SiMe_3$	68%	1 : 99

Mercury Organomercury compounds generally react readily with halogens to give the corresponding organic halides. Although the reaction has been widely used to determine the position of the mercury atom in an organomercurial and investigated throughly from the mechanistic viewpoint,[46] synthetically useful and important reactions are still limited.

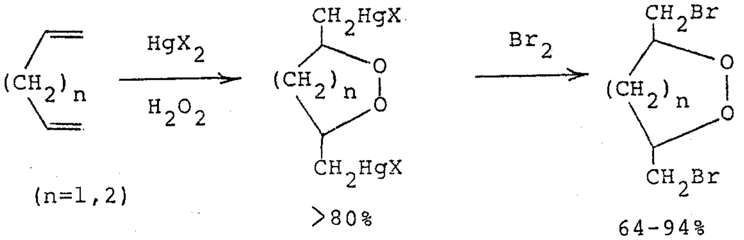
Halogenation of organomercurials prepared by solvomercuration of olefins (usually *trans*-addition) provides a convenient method for the synthesis of various kinds of β-substituted organic bromides[47-50] and iodides[51-53] in high yields (Scheme 26).



$$RCH=CH_2 \xrightarrow[HY]{HgZ_2} \underset{\displaystyle Y}{RCH}CH_2HgZ \longrightarrow \underset{\displaystyle Y}{RCH}CH_2X \qquad (26)$$

Y=OH, OR, OOR; X=Br, I

Some interesting examples of the application of this reaction to the synthesis of brominated cyclic peroxides[54] and bromolactone[55] are shown in Scheme 27 and 28, respectively.



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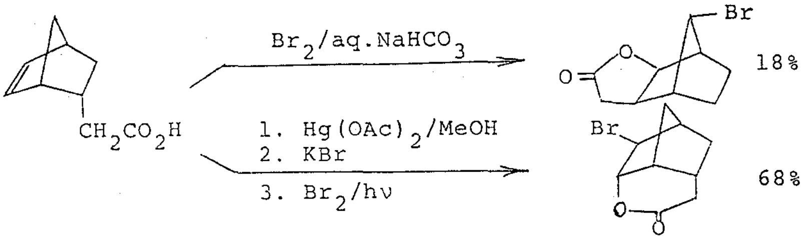
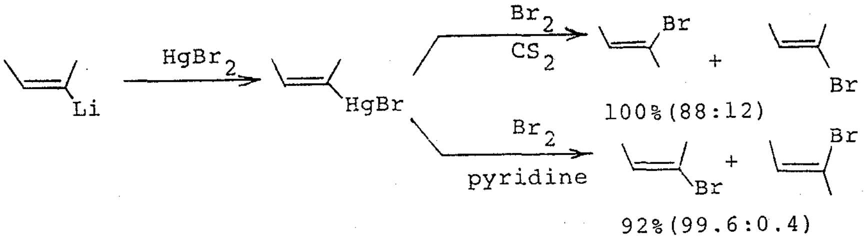


(28)

The C-Hg bond of vinylic mercury compounds can be converted to C-Br and C-I bond by treating with Br$_2$[56,57] and I$_2$,[57,58] respectively. In the bromodemercuration the stereochemistry of the products depends profoundly upon the solvent used and either the retained or inverted vinylic bromide can be obtained simply by changing the solvent as exemplified in Scheme 29.[56] Acetoxymercuration of alkylphenylacetylenes proceeded completely in a *trans* fashion and halogenodemercuration of the produced alkenylmercury compounds occurred completely with reten-



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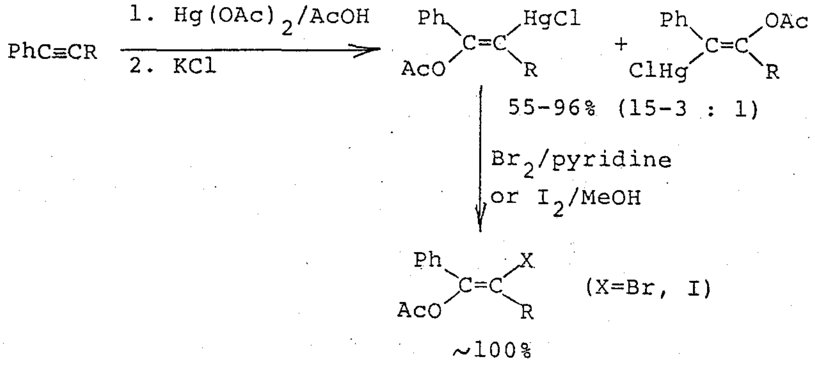
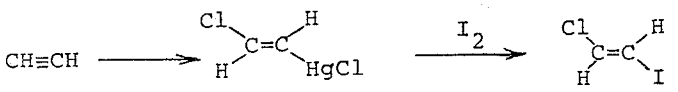
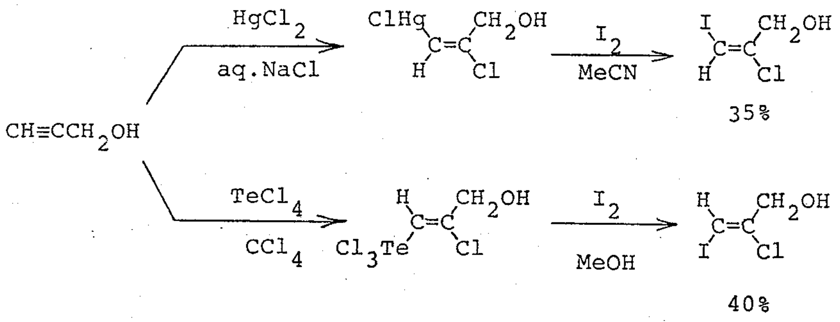


(30)

tion of configuration under the conditions shown in Scheme 30 and afforded the expected halides quantitatively.[57)] The ionic iodination of both *cis*- and *trans*-*β*-chlorovinylmercury (II) chlorides provides a route to the corresponding vinyl iodides (Scheme 31).[58)] In connection with this reaction the addition of $TeCl_4$ to


(31)

acetylenic compounds and iododetelluration of the products should be worth to refer.[59)] It proceeds completely in a *cis*-fashion (Scheme 32 and 33). Halogenodetelluration of aryltellurium compounds is also reported recently, but the synthetically useful example is very limited.[60)]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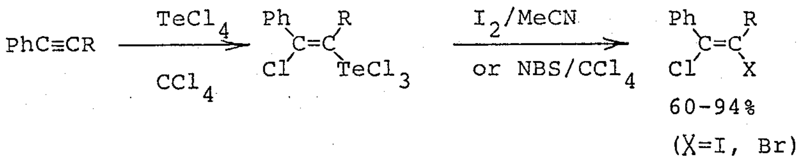
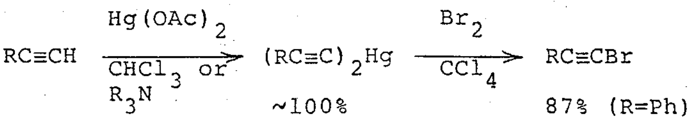

(33)

Acetylenic[61,62)] and aryl halides[63)] can be prepared similarly by the respective halogenodemercuration (Scheme 34 and 35). Mercuration of pyridine occurs mainly at 3-position to give 3-pyridylmercury compounds which affords 3-halogenopyridines almost quantitatively.[64,65)] We recently found that mercury (II) nicotinate reacts with bromine and iodine to give 3-halogenopyridine selectively in moder-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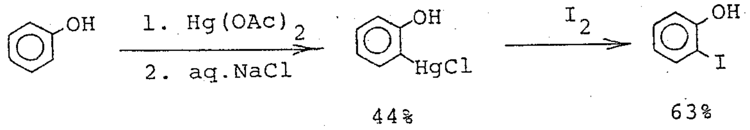
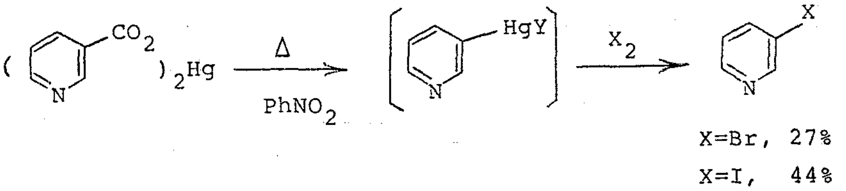

(35)

ate yields, probably *via* pyridylmercury (II) compound produced *in situ* by decarboxylation (Scheme 36).[65]



(36)

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