

HALOMETHYL-METAL COMPOUNDS XXXV*. THE PREPARATION OF DIBROMOMETHYL AND BROMO- CHLOROMETHYL DERIVATIVES OF SILICON AND GERMANIUM BY THE (TRIHALOMETHYL)MERCURIAL ROUTE AND THEIR REDUCTION TO MONOHALOMETHYL COMPOUNDS

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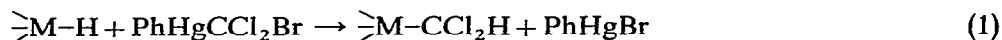
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SUMMARY

The reaction of phenyl(dibromochloromethyl)mercury and phenyl(tribromomethyl)mercury with organosilicon and organogermanium hydrides gave bromochloromethyl- and dibromomethyl-substituted derivatives of silicon and germanium via dihalocarbene insertion into the Si-H and Ge-H bonds. The reduction of these products with tri-n-butyltin hydride at room temperature gave the respective monohalomethyl compounds, the bromochloromethyl derivatives being reduced to the chloromethyl compounds, the dibromomethyl derivatives to the bromomethyl compounds. Excellent yields were obtained in both steps of this new synthesis of monohalomethyl derivatives of silicon and germanium.

INTRODUCTION

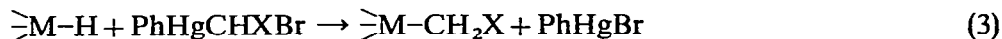
We have reported previously concerning the insertion of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene into Si-H and Ge-H bonds (eqn. 1)². The resulting (dichloromethyl)silanes and -germanes have limited utility, the only



useful reaction of this class of compounds developed thus far being their conversion to lithium reagents (eqn. 2)³. More useful as intermediates in organometallic synthesis



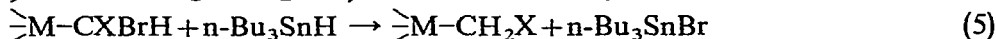
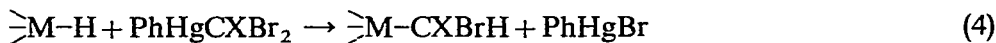
are monohalomethyl compounds of type $\text{R}_3\text{MCH}_2\text{X}$ and $\text{R}_2\text{M}(\text{CH}_2\text{X})_2$ ^{4,5}. In a previous study we had investigated the reactions of phenyl(dihalomethyl)mercury compounds with organosilicon and organogermanium hydrides (eqn. 3)⁶, but had found that they were not preparatively useful except in the case of trialkylsilanes



* For Part XXXIV see ref. 1.

because of the deleterious effects of the high temperatures and long reaction times required on many of the reaction products.

An alternative to the process shown in eqn. (3) would be the two-step procedure shown in eqns. (4) and (5). The reactions of triethyl- and triphenylsilane with phenyl-



(tribromomethyl)mercury had been carried out previously^{2a}, good yields of triethyl- and triphenyl(dibromomethyl)silane being obtained. However, CClBr insertion into Si-H and Ge-H bonds by the mercurial route had not yet been studied. In the present report we describe our work on the reactions summarized by eqns. (4) and (5) which resulted in a useful new synthesis of chloromethyl and bromomethyl derivatives of silicon and germanium.

RESULTS AND DISCUSSION

The expected excellent applicability of phenyl(dibromochloromethyl)mercury to the synthesis of bromochloromethyl derivatives of silicon and germanium has been confirmed and further examples of the preparation of dibromomethyl derivatives of silicon via phenyl(tribromomethyl)mercury have been provided (Table 1). The high yields listed were obtained by heating a benzene solution of the appropriate mercurial with the respective hydride at reflux for 4 h or at 60° for ca. 28 h.

The organotin hydride procedure has been applied previously to the stepwise reduction of polyhalomethanes^{7,8}, and, more to the point, of (trihalomethyl)mercurials^{2a} and (tri- and dichloromethyl)tin compounds⁹. We have found that this procedure serves excellently for the conversion of the dihalomethyl derivatives shown in Table 1, as well as of triethyl- and triphenyl(dibromomethyl)silane, to the respective monochloro- or monobromomethyl compound. A procedure in which the (dihalomethyl)silicon derivative prepared in the first step was not isolated was operationally simpler: filtration of the reaction mixture was followed by treatment of the filtrate with tri-*n*-butyltin hydride. However, in a few cases isolation of the initial insertion product was found to be advisable since the preparation required the use of an excess of mercurial reagent in order to achieve good yields. In these reaction mixtures the C₂Cl₂Br₂ and C₂Br₄ present (derived from decomposition of the excess mercurial) also would be expected to react with the organotin hydride. These reduction reaction mixtures were easily worked up; in some cases a simple fractional distillation of the reaction mixture served to separate the product, but in others prior removal of the tri-*n*-butyltin bromide formed by conversion to the insoluble fluoride¹⁰ was required. The results of these reduction experiments are given in Table 2.

The procedures we describe here are easily carried out and give high product yields. Mono-reduction of the dihalomethyl compounds occurs almost exclusively; little, if any, di-reduction occurs. The required organomercury reagents are easily prepared¹¹ and most of the organosilicon hydrides can be purchased. Tri-*n*-butyltin hydride can be prepared in larger quantities from commercially available bis(tri-*n*-butyltin) oxide ("TBTO", M&T Chemicals, Inc.) using either lithium aluminum hydride¹² or a commercial methylhydropolysiloxane ("Dri-Film 1040", General Electric Co.)¹³ as hydride source. The recent improvement in the procedure which

TABLE 1

PREPARATION OF DIHALOMETHYL COMPOUNDS OF SILICON AND GERMANIUM

Starting hydride ^a	Product and yield (%)	B.p. [^o C(mm)] or m.p. (^o C)	<i>n</i> _D ²⁵	δ (CXYH) (ppm) ^b	Analysis, found (calcd.)	
					(%)	(%)
Et ₃ SiH	Et ₃ SiCClBrH (81)	b.p. 34 ^o (0.05)	1.4870	5.32	34.66 (34.50) ⁱ	6.53 (6.62)
Ph ₃ SiH	Ph ₃ SiCClBrH (86)	m.p. 149–150.5 ^o		5.84	58.99 (58.84)	4.30 (4.16)
Et ₂ SiH ₂	Et ₂ HSiCClBrH (72) ^f	GLPC isolation	1.4842	5.31 d (<i>J</i> 2 Hz)	28.02 (27.85)	5.67 (5.61)
Ph ₂ SiH ₂	Ph ₂ HSiCClBrH (71) ^d	GLPC isolation	1.6100	5.54 d (<i>J</i> 2 Hz)	50.36 (50.10)	3.98 (3.85)
Me ₂ (CH ₂ Cl)SiH	Me ₂ (CH ₂ Cl)SiCClBrH (91)	GLPC isolation	1.5008	5.40 ^g	20.53 (20.35)	3.93 (3.84)
Ph ₃ GeH	Ph ₃ GeCClBrH (73)	m.p. 143–145 ^o		5.80	52.79 (52.79)	3.78 (3.73)
Et ₂ SiH ₂ ^a	Et ₂ HSiCBr ₂ H (80) ^e	GLPC isolation	1.5119	5.20 d (<i>J</i> 2 Hz)	23.89 (23.09)	4.57 (4.65)
Ph ₂ SiH ₂ ^a	Ph ₂ HSiCBr ₂ H (61) ^f	m.p. 47.5–48.5 ^o		5.38 d (<i>J</i> 2 Hz)	43.84 (43.85)	3.43 (3.37)
Me ₂ (CH ₂ Cl)SiH ^a	Me ₂ (CH ₂ Cl)SiCBr ₂ H (80)	GLPC isolation	1.5270	5.28 ^h	17.21 (17.13)	3.22 (3.23)

^a The mercurial used was PhHgCClBr₂ except in the last three cases where PhHgCBr₃ was used. ^b In CCl₄ solution. ^c ν (Si-H) 2130 cm⁻¹. ^d ν (Si-H) 2160 cm⁻¹. ^e ν (Si-H) 2110 cm⁻¹. ^f ν (Si-H) 2150 cm⁻¹. ^g δ (CH₂Cl) 2.94 ppm. ^h δ (CH₂Cl) 2.94 ppm. ⁱ Cl: found 14.40, calcd. 14.55; Br: found 32.61, calcd. 32.80%.

uses the latter reagent¹⁴ should be applicable to the present systems. Thus for the laboratory-scale preparation of halomethyl compounds of silicon and germanium of the types shown in Tables 1 and 2 these procedures can be used to good advantage.

EXPERIMENTAL

General comments

All reactions were carried out under an atmosphere of prepurified nitrogen in acid-washed, flame-dried glassware. Infrared spectra of all compounds prepared in this study were recorded using a Perkin-Elmer Model 237B Infracord spectrophotometer, NMR spectra using a Varian Associates A60 or T60 spectrometer. Chemical shifts are recorded in δ units in ppm downfield from TMS. Gas-liquid partition chromatography (GLPC) often was used in product separation, isolation and yield analysis. M.I.T. isothermal units and F&M Model 700 and 720 gas chromatographs were used. Mostly columns were packed with 20% General Electric Co. SE-30 silicone rubber gum or Dow Corning DC 200 silicone fluid on Chromosorb W; in some cases a more polar liquid phase, General Electric Co. XE-60 or XF-1150, was used. Yield determination was performed using the internal standard procedure.

TABLE 2

REDUCTION OF DIHALOMETHYL COMPOUNDS OF SILICON AND GERMANIUM

Starting compound	Procedure	Product	Yield (%) ^a
Et ₃ SiH	via Et ₃ SiCClBrH without isolation	Et ₃ SiCH ₂ Cl	74
Et ₃ SiH	via Et ₃ SiCBr ₂ H without isolation	Et ₃ SiCH ₂ Br	79
Ph ₃ SiH	via Ph ₃ SiCClBrH without isolation	Ph ₃ SiCH ₂ Cl	81
Ph ₃ SiH	via isolated Ph ₃ SiCBr ₂ H	Ph ₃ SiCH ₂ Br	76 ^b
Ph ₃ GeH	via isolated Ph ₃ GeCClBrH	Ph ₃ GeCH ₂ Cl	56 ^c
Me ₂ (CH ₂ Cl)SiH	via Me ₂ (CH ₂ Cl)SiCClBrH without isolation	Me ₂ Si(CH ₂ Cl) ₂	81
Me ₂ (CH ₂ Cl)SiH	via Me ₂ (CH ₂ Cl)SiCBr ₂ H without isolation	Me ₂ Si(CH ₂ Cl)CH ₂ Br	86
Et ₂ SiH ₂	via Et ₂ HSiCClBrH without isolation	Et ₂ HSiCH ₂ Cl	76
Et ₂ SiH ₂	via Et ₂ HSiCBr ₂ H without isolation	Et ₂ HSiCH ₂ Br	65

^a Over-all yield, based on starting hydride. ^b Insertion yield 89%; reduction yield 85%. ^c Insertion yield 73%; reduction yield 77%.

The progress of the mercurial/hydride reactions was followed by thin-layer chromatography (TLC)¹⁵. The organomercury reagents were prepared using our recently reported procedure¹¹. Most of the silicon hydrides were purchased from Alfa Inorganics, Inc., or Peninsular ChemResearch, Inc. Others were prepared by the standard lithium aluminum hydride reduction of the respective chlorosilane in diethyl ether solution. Tri-*n*-butyltin hydride was prepared by the reduction of bis(tri-*n*-butyltin) oxide^{12,13}.

Preparation of the (dihalomethyl)silanes and -germanes

The general procedure described for the organosilicon hydride/phenyl(bromodichloromethyl)mercury reaction^{2a} was followed. In a three-necked flask of appropriate size equipped with a reflux condenser topped with a nitrogen inlet tube and a magnetic stirring assembly was charged a mixture of the mercurial (PhHgCClBr₂ or PhHgCBr₃), one to three molar equivalents of the Group IV hydride and dry benzene (ca. 25 ml for a 50 mmol mercurial reaction). The mixture was stirred and heated (2–4 h at reflux or 28 h at 60°) under nitrogen. The reaction mixture was filtered to remove the precipitated phenylmercuric bromide (usually in greater than 90% yield). The filtrate was trap-to-trap distilled at reduced pressure (0.05–2 mm) into a receiver at –78° and then the filtrate was analyzed by GLPC. Alternatively, the filtrate was vacuum-distilled using a Vigreux column of appropriate length. In the cases of the Ph₃MCX₂H compounds the filtrate was evaporated and the residue crystallized from carbon tetrachloride/hexane mixtures. With the Ph₃MH compounds the use of an excess of hydride would have made such work-up difficult. Accordingly, these reactions were carried out using 1 mole of mercurial per 1 mole of Ph₃MH. With such

stoichiometry, some hydride usually remained after all of the mercurial had been consumed and more mercurial was added (25–50% excess). After the hydride had been completely consumed (as shown by TLC or IR), the remaining mercurial was destroyed by adding cyclohexene and refluxing for another hour. The compounds prepared by this procedure are listed in Table 1.

Reduction of the (dihalomethyl)silanes and -germanes to the respective monohalomethyl compounds

The procedure used for the mono-reduction of *gem*-dibromo- or bromochloro-cyclopropanes⁷ was applicable. The filtrate from an organosilicon or organogermanium hydride/PhHgCXBr₂ (X = Cl or Br) reaction was charged into a three-necked flask equipped with a magnetic stirring unit, a pressure-equalizing addition funnel and a reflux condenser topped with a nitrogen inlet tube. An equimolar quantity of tri-*n*-butyltin hydride then was added slowly with stirring at room temperature and the resulting reaction mixture was stirred another 12 h at room temperature.

In most cases the tri-*n*-butyltin bromide which had been formed was removed by converting it to tri-*n*-butyltin fluoride. The reaction mixture was transferred to an Erlenmeyer flask and a solution of 10% KF in 1/1 water/ethanol (ca. 200 ml for a 50 mmole reaction) was added. This caused precipitation of a gelatinous mass which was rendered filterable by shaking with 200 ml of acetone. Filtration then removed tri-*n*-butyltin fluoride, dec. 255–265°. The dried organic phase, after appropriate extractions of it with water and of the aqueous phase with benzene, was either vacuum-distilled to obtain the monohalomethyl product or was analyzed by GLPC. In some cases [e.g., the Me₂Si(CH₂Cl)(CH₂X) compounds] the tri-*n*-butyltin bromide was not removed in this manner. Instead, the reaction mixture was trap-to-trap distilled in vacuum to leave behind the tri-*n*-butyltin bromide as a residue. The product then was obtained from the distillate by another fractional distillation or, more usually, the distillate was analyzed by GLPC.

In the preparation of Ph₃SiCH₂Cl, Ph₃SiCH₂Br and Ph₃GeCH₂Cl the reactions were carried out by allowing the pure, isolated Ph₃MCXBr₂ compound to

TABLE 3

(MONOHALOMETHYL)SILANES AND -GERMANES PREPARED

Compound	B.p. [°C (mm)] or m.p. (°C)		n_D^{25}		$\delta(\text{CH}_2\text{X})$ (ppm)
	Observed	Lit. [ref.]	Observed	Lit. [ref.]	
Et ₃ SiCH ₂ Cl	b.p. 97–100° (60)	116° (100) [16]	1.4462	1.4452 [17]	2.70
Et ₃ SiCH ₂ Br	b.p. 78–79° (15)		1.4660	1.4672 [6]	2.38
Ph ₃ SiCH ₂ Cl	m.p. 114–116°	112° [18]			3.40
Ph ₃ GeCH ₂ Cl	m.p. 118–120.5°	117.5–118.5 [19]			3.84
Ph ₃ SiCH ₂ Br	m.p. 118–121.5°	121–122.5 [20]			3.06
Me ₂ Si(CH ₂ Cl) ₂	GLPC isolation		1.4580	1.4579 [21]	2.90
Me ₂ Si $\begin{matrix} \text{CH}_2\text{Cl} \\ \text{CH}_2\text{Br} \end{matrix}$	GLPC isolation ^a		1.4838		{ 2.90 (CH ₂ Cl) 2.56 (CH ₂ Br)
Et ₂ HSiCH ₂ Cl	GLPC isolation		1.4357	1.4357 [22]	2.84 d (J 2 Hz)
Et ₂ HSiCH ₂ Br	GLPC isolation		1.4654		2.42 d (J 2 Hz)

^a Found: C, 23.96; H, 4.99. Calcd: C, 23.83; H, 5.00.

react with a molar equivalent of tri-n-butyltin hydride in pentane at room temperature. Ca. 10 ml of solvent was used in a 10 mmole reaction; under these conditions most of the product crystallized from solution. A smaller second crop could be obtained by concentration of the reaction mixture.

The halomethyl compounds prepared by this reduction reaction are listed in Table 3.

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