Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

HALOMETHYL-METAL COMPOUNDS
X[a]. THE REACTION OF ORGANOSILICON, ORGANOGERMANIUM AND ORGANOTIN HYDRIDES WITH PHENYL(TRIHALOMETHYL)MERCURY COMPOUNDS[b]

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(Received July 1st, 1966)

During our initial studies of the reactions of phenyl(trihalomethyl)mercury compounds, which we had found to be powerful reagents for the synthesis of *gem*-dihalocyclopropanes from olefins[4], it was discovered that phenyl(bromodichloromethyl)mercury and phenyl(tribromomethyl)mercury were capable of inserting CCl_2 and CBr_2, respectively, into aliphatic C–H bonds[2]. Our long-standing interest in the organometallic chemistry of silicon, germanium and tin made it of interest to investigate the possible insertion of CX_2 into the Si–H, the Ge–H and the Sn–H bonds using these organomercury reagents. Accordingly, we carried out reactions of organosilicon, organogermanium and organotin hydrides with phenyl(trihalomethyl)mercurials.

ORGANOSILICON AND ORGANOGERMANIUM HYDRIDES

When a benzene solution of phenyl(bromodichloromethyl) mercury and an organosilicon or an organogermanium hydride was heated at reflux, phenylmercuric bromide began to precipitate, and within two hours the starting mercurial had been consumed completely. Work-up of the reaction mixture showed that (dichloromethyl)-silicon or (dichloromethyl)germanium derivatives had been produced in high yields, *e.g.*, eqn. (1) and (2).

$$(C_6H_5)_3SiH + C_6H_5HgCCl_2Br \rightarrow (C_6H_5)_3SiCCl_2H\ (90\%) + C_6H_5HgBr$$

$$(C_6H_5)_3GeH + C_6H_5HgCCl_2Br \rightarrow (C_6H_5)_3GeCCl_2H\ (88\%) + C_6H_5HgBr$$

Dichloromethylenation of diphenylsilane could be carried out stepwise; use of the silane and phenyl(bromodichloromethyl)mercury in 1 : 1 molar ratio gave

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[a] Part IX of this series: ref. 1.
[b] Preliminary communications: ref. 2 and 3.
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$(C_6H_5)_2HSiCCl_2H$, while use of an excess of mercurial resulted in formation of $(C_6H_5)_2Si(CCl_2H)_2$. The reaction of triphenylsilane with phenyl(tribromomethyl)-mercury gave $(C_6H_5)_3SiCBr_2H$ (65%). The (dihalomethyl)silanes and -germanes which were prepared, together with the physical properties which characterize them are listed in Table 1. Their NMR spectra, which showed the $SiCX_2H$ and $GeCX_2H$ protons at *ca.* $\delta = 5.25$–6.0 ppm downfield from tetramethylsilane, were especially useful in their characterization.

TABLE 1

(DIHALOMETHYL)SILICON AND -GERMANIUM COMPOUNDS

Compound	*M.p. (°C) or b.p. (°C/mm Hg)*	$n^{25}D$	$\delta(CX_2H)^a$
$(C_6H_5)_3SiCCl_2H$	M.p. 151–152		6.0
$(C_2H_5)_3SiCCl_2H$	B.p. 97–99/25	1.4658	5.44
$(C_6H_5)_2HSiCCl_2H$	B.p. 118–119/0.4	1.5942	5.70[b]
$(C_6H_5)_2Si(CCl_2H)_2$	M.p. 100–102		6.08
$(C_6H_5)_2(CH_2{=}CH)SiCCl_2H^c$	(isolated by g.l.c.)	1.5905	5.66
$(C_6H_5)_3SiCBr_2H$	M.p. 154–156		5.72
$(C_2H_5)_3SiCBr_2H$	(isolated by g.l.c.)		5.23
$(C_6H_5)_3GeCCl_2H$	M.p. 154–155		5.95
$(C_2H_5)_3GeCCl_2H$	(isolated by g.l.c.)	1.4798	5.42

[a] In ppm downfield from tetramethylsilane. [b] Doublet, $J = 2.5$ cps (splitting due to Si–H). [c] $\nu(C{=}C)$ at 1595 cm^{-1}; vinyl proton absorption at 5.7–7.2 ppm.

This procedure thus provides a useful, general route to the preparation of dihalomethyl derivatives of silicon and germanium. (Dichloromethyl)silicon compounds had been prepared previously by chlorination of methylsilanes[5], and (dihalomethyl)germanes were unknown prior to this study.

Since these dihalomethylenations of Si–H and Ge–H linkages occurred under conditions identical to those used in the $C_6H_5HgCX_2Br$ + olefin reactions[4], it was of interest to determine the relative reactivities of organosilicon and organogermanium hydrides with respect to olefins. Competition experiments were carried out in which equimolar amounts of cyclohexene and triethylsilane were allowed to compete for a deficiency of $C_6H_5HgCCl_2Br$ in benzene at 80°. The relatives rate was calculated by the formula[6]:

$$k_{rel} = \frac{k(Et_3SiH)}{k(C_6H_{10})} = \frac{P(Et_3SiH)}{P(C_6H_{10})} \times \frac{O(C_6H_{10})}{O(Et_3SiH)}$$

where k = the rate constant for the reaction in question, P = product yield in millimoles derived from the respective starting material and O = millimoles used of the respective starting material. For triethylsilane k_{rel} thus defined was determined to be 0.805. Thus in contrast to the C–H linkage, the Si–H bond equals olefins in its reactivity toward mercurial-derived CCl_2. In an experiment in which triethylsilane and triethylgermane were allowed to compete for a deficiency of phenyl(bromodichloromethyl)mercury, it was determined that the germanium hydride is about 4.5 times more reactive than the silicon hydride. These relative rates are meaningful only if the kinetic order of the hydride in its reaction with the mercurial is the same as the kinetic order of cyclohexene in its reaction with the mercury compound. It is possible to test for this requirement by means of variable concentration experiments. If the k_{rel} value remains unchanged while the relative concentrations of the competing reagents are changed, then this requirement is met, provided the rates in question do not approach the diffusion-controlled limiting values. Table 2 shows the results of such variable concentration competition experiments. In these runs ordinary magnetic stirring was used. An identical series of experiments was carried out using high-speed stirring, and essentially the same results were obtained. The constancy of k_{rel} (within experimental error) in these experiments allows one to conclude that the order of the $C_6H_5HgCCl_2Br+Et_3MH$ reaction and the $C_6H_5HgCCl_2Br$+cyclohexene reaction are the same. Since we have shown that the inital rate of the cyclooctene+$C_6H_5HgCCl_2Br$ reaction is first order in mercurial and zero order in olefin[7], the results obtained would indicate that in the Group IV hydride+mercurial reaction we are dealing with a process in which a rate-determining, monomolecular, reversible decomposition of the phenyl(trihalomethyl)mercurial is followed by a rapid insertion of CCl_2 into the Si–H or Ge–H bond (eqn. 3 and 4). Independent confirmation is being sought by means of a kinetic study of the triethylsilane + phenyl(bromodichloromethyl)mercury reaction. The nature of this CCl_2 insertion into the Si–H and Ge–H bond is not yet well understood. The reaction has been shown to be stereospecific by Sommer and Ritter[8]. These workers found that the reaction of phenyl(tribromomethyl)mercury with optically active α-naphthylphenylmethylsilane produced optically active α-naphthylphenylmethyl(dibromomethyl)silane with unchanged configuration. This fact could be taken to speak for a transition state, (I), of the type suggested by Doering and Prinzbach[9] for CH_2 insertion into C–H bonds.

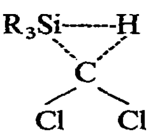
TABLE 2

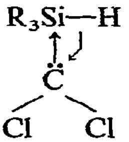
COMPETITION EXPERIMENTS: TRIETHYLSILANE *vs.* CYCLOHEXENE AND TRIETHYLSILANE *vs.* TRIETHYLGERMANE FOR PHENYL(BROMODICHLOROMETHYL)MERCURY

O(Et_3SiH) (*mmoles*)	*O*(*cyclohexene*) (*mmoles*)	*P*(Et_3SiH) (*mmoles*)	*P*(*cyclohexene*) (*mmoles*)	*Total yield* (%)	*k*(Et_3SiH)/*k*(*cyclohexene*)
25.0	25.0	1.91	2.36	95.4	0.805
25.0	50.0	1.14	2.85	79.8	0.800
50.0	25.0	2.88	1.81	93.8	0.796
25.0	25.0 (Et_3GeH)	0.852	3.86 [*P*(Et_3GeH)]	94.2	4.53 [*k*(Et_3GeH)/*k*(Et_3SiH)]

$$C_6H_5HgCCl_2Br \rightleftharpoons C_6H_5HgBr+CCl_2 \quad (\text{or } C_6H_5HgBr\cdot CCl_2) \qquad (3)$$

$$CCl_2 \quad (\text{or } C_5H_5HgBr\cdot CCl_2)+(C_2H_5)_3SiH \rightarrow (C_2H_5)SiCCl_2H \quad (+C_6H_5HgBr) \qquad (4)$$


(I)


(II)

However, one can conceive of nucleophilic attack by CCl_2 at silicon (II) as an alternate possibility which could (but need not) proceed with retention of configuration at silicon. It may be noted that we have discussed the possibility of nucleophilic reactions of CCl_2 with suitable substrates in previous papers[7,10]. Either of these possibilities, (I) or (II), would accomodate the experimentally observed greater reactivity of triethylgermane as compared with triethylsilane. Experimental studies are currently in progress which hopefully will allow us to say something more definite about the nature of these insertion reactions.

One possible route to the observed products of the $(C_2H_5)_3SiH+C_6H_5HgCCl_2Br$ reaction which we considered to be less likely than CX_2 insertion into the Si–H bond, but which nevertheless had to be examined experimentally, was a sequence of reduction and substituent exchange (eqn. 5 followed by 6). Such a mechanism was

$$(C_2H_5)_3SiH+C_6H_5HgCCl_2Br \rightarrow (C_2H_5)_3SiBr+C_6H_5HgCCl_2H \qquad (5)$$

$$(C_2H_5)_3SiBr+C_6H_5HgCCl_2H \rightarrow (C_2H_5)_3SiCCl_2H+C_6H_5HgBr \qquad (6)$$

excluded by the fact that triethylbromosilane and phenyl(dichloromethyl)mercury do not react under the conditions used in the dichloromethylenation reaction under discussion[3].

Since triethylsilane was found to be *ca.* 0.8 as reactive as cyclohexene toward CCl_2 as generated via phenyl(bromodichloromethyl)mercury, it was predicted that trialkylvinylsilanes, which have been shown to be extremely poorly reactive toward CCl_2 as generated by the Doering–Hoffmann procedure[11], *via* $C_6H_5HgCCl_2Br$[12] and via CCl_3SiCl_3[13], would not be able to compete effectively with triethylsilane in a competition experiment for a deficiency of phenyl(bromodichloromethyl)-mercury. This was found to be the case. A competition of 0.03 mole each of triethylsilane and triethylvinylsilane for 0.01 mole of $C_6H_5HgCCl_2Br$ resulted in exclusive formation of (dichloromethyl)triethylsilane. No 1,1-dichloro-2-(triethylsilyl)cyclopropane[4] was observed. This large reactivity difference between a silicon hydride and a vinylsilane allowed the synthesis of (dichloromethyl)diphenylvinylsilane from diphenylvinylsilane in 82% yield (eqn. 7).

$$(C_6H_5)_2(CH_2{=}CH)SiH+C_6H_5HgCCl_2Br \rightarrow (C_6H_5)_2(CH_2{=}CH)SiCCl_2H + C_6H_5HgBr \qquad (7)$$

It should be mentioned that phenyl(trihalomethyl)mercurials are not unique in their ability to insert CX_2 into the Si–H bond. As we have reported previously[14], the decarboxylation of sodium trichloroacetate in 1,2-dimethoxyethane solution in the presence of triethylsilane gave (dichloromethyl)triethylsilane in 32% yield.

The mercurial route also allows preparation of monohalomethylsilanes and methylsilanes from Si–H compounds (eqn. 8 and 9). Details concerning these and related reactions will be reported in a subsequent paper.

$$C_6H_5HgCBr_2H+(C_2H_5)_3SiH \rightarrow (C_2H_5)_3SiCH_2Br+C_6H_5HgBr \quad \text{(ref. 15)} \qquad (8)$$

$$ICH_2HgI+(C_6H_5)_2Hg+(C_2H_5)_3SiH \rightarrow (C_2H_5)_3SiCH_3+2\ C_6H_5HgI \quad \text{(ref. 2)} \qquad (9)$$

ORGANOTIN HYDRIDES

At first sight, one might expect that the reaction of a trialkyltin hydride with phenyl(bromodichloromethyl)mercury might provide a (dichloromethyl)trialkyltin compound by CCl_2 insertion into the Sn–H bond. However, in contrast to trialkylsilicon and trialkylgermanium hydrides, the trialkyltin hydrides are powerful reagents for the reduction of organic halides[16]. In our own experience, we have noted[17] the facile reduction of bromoform and tribromofluoromethane to dibromomethane and dibromofluoromethane, respectively, by the action of tri-n-butyltin hydride at 0°. Kuivila and coworkers have shown that such reductions occur by a radical chain mechanism involving R_3Sn radicals[18]. It therefore was not surprising that tri-n-butyltin hydride and phenyl(bromodichloromethyl)mercury reacted in benzene solution at room temperature as shown in eqn. 10. After removal of tri-n-butyltin

$$(C_4H_9)_3SnH + C_6H_5HgCCl_2Br \rightarrow C_6H_5HgCCl_2H + (C_4H_9)_3SnBr \qquad (10)$$

bromide as the insoluble fluoride by addition of aqueous–alcoholic KF solution, phenyl(dichloromethyl)mercury was isolated in yields of usually 40–50%. In some instances yields as high as 85% were obtained. Triphenyltin hydride reacted in similar fashion.

Attempts to prepare phenyl(bromochloromethyl)mercury and phenyl(dibromomethyl)mercury by the reactions shown in equations 11 and 12 were less successful. Oils which could not be crystallized were obtained in most cases, and the

$$(C_4H_9)_3SnH + C_6H_5HgCClBr_2 \rightarrow C_6H_5HgCBrClH + (C_4H_9)_3SnBr \qquad (11)$$

$$(C_4H_9)_3SnH + C_6H_5HgCBr_3 \rightarrow C_6H_5HgCBr_2H + (C_4H_9)_3SnBr \qquad (12)$$

maximum yields, obtained in isolated cases when partial crystallization could be achieved, were *ca.* 20% of crude solid product. Recrystallization of these solids led to pure products characterized as the desired (dihalomethyl)mercurials. These results most likely are due to the lack of selectivity of tri-n-butyltin radical attack on starting material and the desired product, both of which contain C–Br linkages. It is to be noted that C–Cl bonds are much less readily reduced by organotin hydrides than are C–Br bonds[16,17], hence the isolation of $C_6H_5HgCCl_2H$ in moderate to high yields is understandable. This procedure for the preparation of phenyl(dihalomethyl)-mercury compounds thus is considerably less practical than the reaction of phenylmercuric halide, dihalomethane and potassium tert-butoxide[3,19].

Platinum(II) hydrides, *e.g.*, *trans*-$(Et_3P)_2PtHCl$, which are known to reduce organic halides, also reduced phenyl(bromodichloromethyl)mercury[20]. No products of CCl_2 insertion into the Pt–H bond could be detected.

EXPERIMENTAL

General comments

All experiments were performed under an atmosphere of prepurified nitrogen. Gas-chromatographic analyses were carried out using an M.I.T. isothermal unit (20% General Electric SE 30 Silicone Rubber Gum on Chromosorb W or 25% Dow Corning 710 Silicone Oil on Chromosorb P) or an F&M 700 temperature-programmed gas chromatograph (20% SE 30 on Chromosorb W). The progress of phenyl-(trihalomethyl)mercury reactions was monitored by thin-layer chromatography[21].

Infrared spectra were recorded using a Baird Model B or Perkin Elmer Infracord 237 or 337 infrared spectrophotometer and were taken of pure liquids. Proton resonance spectra were obtained in carbon tetrachloride solution with a

Varian Associates A-60 NMR spectrometer. Chemical shifts are given in ppm downfield from tetramethylsilane.

Elemental analyses were performed by Dr. S. M. Nagy, M.I.T. Microchemical Laboratory, by the Galbraith Laboratories, Knoxville, Tenn., or by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Phenyl(trihalomethyl)mercury compounds[21], triethylgermane[22], triphenylgermane[23], tri-n-butyltin hydride[24] and triphenyltin hydride[25] were prepared by literature procedures. Triethylsilane, triphenylsilane and diphenylsilane were purchased from Peninsular ChemResearch, Inc.

Reaction of phenyl(trihalomethyl)mercury compounds with organosilicon and organogermanium hydrides

The preparations of (dichloromethyl)triethylsilane (a liquid) and (dichloromethyl)triphenylgermane (a solid) are described to illustrate the procedures used.

(Dichloromethyl)triethylsilane. Into a dry 100-ml three-necked flask, equipped with a magnetic stirring unit and a reflux condenser, was charged 22.0 g (0.05 mole) of phenyl(bromodichloromethyl)mercury, 23.8 ml (0.015 mole) of triethylsilane (b.p. 107–108.5°) and 50 ml of benzene, under an argon atmosphere. The mixture was stirred and heated (bath temperature 85–90°) for 2 h. Precipitation of phenylmercuric bromide was observed. The reaction mixture was cooled and filtered from 17.1 g (96%) of phenylmercuric bromide, m.p. 283–285°. The filtrate was separated by trap-to-trap distillation at 0.2 mm into a low (25°) and a high (25–80°) boiling fraction to remove the solvent. A final short path distillation of the latter afforded 7.9 g (79%) of a clear liquid, b.p. 96–99° (25 mm), n_D^{25} 1.4658. Because of the apparent sensitivity of the product to traces of base, it was necessary to use acid-washed distillation equipment and storage vials to obtain a sample that was not cloudy.

Identification of the product as (dichloromethyl)triethylsilane was made by means of its infrared spectrum, which showed no Si–H band at 2100 cm^{-1}, but which had absorptions at 2900(s), 1460(s), 1405(s), 1372(m), 1240(s), 1198(m), 1133(m), 1012(s), 976(m), 800(s), 740(s), and 700(s) cm^{-1}, and by its NMR spectrum, which consisted of two absorptions: a complex ethyl group centered at 0.95 ppm (15H)

TABLE 3

(DIHALOMETHYL)SILICON AND -GERMANIUM COMPOUNDS: YIELDS AND ANALYTICAL DATA

Compound	*Yield* (%)	*Analysis: found (calcd.) (%)* Carbon	*Hydrogen*	*Halogen*	*Metal*
$(C_6H_5)_3SiCCl_2H$	90	66.39 (66.46)	4.45 (4.69)	20.81 (20.65)	8.12 (8.18)
$(C_2H_5)_3SiCCl_2H$	79	42.56 (42.20)	8.22 (8.09)	35.88 (35.59)	
$(C_6H_5)_2HSiCCl_2H$	77[a]	58.34 (58.42)	4.60 (4.53)	26.47 (26.53)	
$(C_6H_5)_2Si(CCl_2H)_2$	72[b]	48.12 (48.02)	3.57 (3.45)	40.20 (40.50)	
$(C_6H_5)_2(CH_2{=}CH)SiCCl_2H$	82[c]	61.91 (61.42)	5.01 (4.81)	24.29 (24.18)	
$(C_6H_5)_3SiCBr_2H$	65	52.70 (52.78)	3.96 (3.73)	37.12 (36.97)	6.18 (6.50)
$(C_2H_5)_3SiCBr_2H$	65[c]	29.27 (29.18)	5.61 (5.59)		
$(C_6H_5)_3GeCCl_2H$	88	58.91 (58.83)	4.41 (4.15)	18.51 (18.28)	19.06 (18.71)
$(C_2H_5)_3GeCCl_2H$	83[c]	34.62 (34.50)	6.34 (6.62)	29.78 (29.09)	

[a] Mercurial to silane ratio used = 1. [b] Mercurial to silane ratio used = 3. [c] Yield determined by g.l.c.; all other yields represent of isolated product.

and a dichloromethyl singlet at 5.44 ppm (1H). The elemental analysis was satisfactory (see Table 3).

(Dichloromethyl)triphenylgermane. The same procedure was used in the reaction of 11 mmoles of $C_6H_5HgCCl_2Br$ with 10 mmoles of triphenylgermane in 20 ml of benzene during 1.3 h. The resulting suspension was filtered from 3.82 g (97%) of phenylmercuric bromide, m.p. 284–286°. The solvent was removed from the filtrate by trap-to-trap distillation at 25° (0.1 mm), leaving 4.45 g of a finely crystalline powder, m.p. 138–146°. The phenyl(bromodichloromethyl)mercurial remaining (as shown by thin-layer chromatography) was removed by sublimation at 55° (0.001 mm). The residue, 3.85 g, m.p. 147–150°, was recrystallized from carbon tetrachloride and n-hexane/carbon tetrachloride mixture to give 3.40 g (88%) of (dichloromethyl)triphenylgermane, m.p. 153–154.5°. An analytical sample had m.p. 154–155°. The proton resonance spectrum of the product showed complex phenyl absorption centered at 7.5 ppm and a dichloromethyl singlet at 5.95 ppm. The infrared spectrum (KBr) showed no Ge–H absorption at 2040 cm^{-1}, but had absorptions at 3100 (w), 1485(m), 1426(m), 1185(w), 1095(m), 1027(w), 1000(w), 748(m), 735(s), 710(m) and 695(s) cm^{-1}. The elemental analysis was satisfactory (Table 3).

Yields obtained in these reactions, together with analytical data for the products, are given in Table 3. The infrared and proton resonance spectra of these compounds are recorded in the Ph.D. theses of J.M.B. (1965) and H.D. (1966).

Competition experiments

The experiment in which equimolar amounts of triethylsilane and cyclohexene were allowed to compete for a deficiency of phenyl(bromodichloromethyl)mercury is described as an example of the procedure used.

A solution of 5 mmoles of $C_6H_5HgCCl_2Br$ and 25 mmoles each of triethylsilane and cyclohexene in 10 ml of dry benzene was heated at 80° for 4 h, under an atmosphere of prepurified nitrogen. The temperature was controlled to ±0.5°. The mixture then was allowed to cool and was filtered to remove 1.78 g (99.5%) of phenylmercuric bromide. The filtrate was used directly for product yield determinations. Ethylbenzene was used as internal standard. Yields were determined using an F&M Model 700 Gas Chromatograph, temperature programmed 60–250°, 10° per min, 50 ml per min helium flow rate. The injection port temperature was 200°, the detector temperature 250°. The g.l.c. column used was 20% General Electric Co. SE-30 on Chromosorb W. The applicability of this analytical technique was confirmed by analysis of synthetic mixtures of (dichloromethyl)triethylsilane and 7,7-dichloronorcarane. The yield of (dichloromethyl)triethylsilane was 1.91 mmoles (38.2%), of 7,7-dichloronorcarane, 2.36 mmoles (47.2%).

Reactions of tri-n-butyltin hydride with phenyl(trihalomethyl)mercury compounds

These reactions are merely descriptive of those preparations from which maximum yields of product were obtained, and, as mentioned in the discussion section, are by no means typical of all attempts to produce phenyl(dihalomethyl)mercury compounds by this means. The physical properties, spectroscopic data and elemental analyses of $C_6H_5HgCCl_2H$, $C_6H_5HgCBrClH$ and $C_6H_5HgCBr_2H$ are given in ref. 3.

Reaction with phenyl(bromodichloromethyl)mercury. Nine g (0.021 mole) of phenyl(bromodichloromethyl)mercury, 130 ml of dry benzene and 30 ml of pentane in a 500-ml three-necked flask equipped with mechanical stirrer and pressure-equalizing dropping funnel, and maintained under an atmosphere of prepurified nitrogen, were cooled with an ice bath. To this mixture was added a solution of 6.0 g (0.021 mole) of tri-n-butyltin hydride in 7 ml of benzene over a one-hour period. The reaction mixture was stirred for an additional hour; the ice bath then was removed and the mixture was left to stand overnight. The resulting clear solution was filtered from a small amount of elemental mercury and treated with 60 ml of a 10% solution of potassium fluoride in a 1 : 1 (vol.) ethanol/water mixture. The reaction mixture, which had become thick and gelatinous, was rendered normally fluid by addition of 50 ml of anhydrous acetone. The two phase supernatant solution was filtered from 5.7 g (91%) of tri-n-butyltin fluoride. The aqueous phase was washed with benzene and the extracts added to the organic layer. The latter then was dried and evaporated under reduced pressure to leave 6.9 g of light gray solid, m.p. 56–64°, which represents a 93% crude yield of phenyl(dichloromethyl)mercury. The crude solid was treated with 150 ml of 4 : 1 n-hexane/chloroform mixture, filtered from 0.2 g of insoluble solid and chilled to give 4.2 g of large, colorless needles, m.p. 69–71°. Concentrating and chilling the mother liquor produced another 1.1 g of solid, m.p. 65–67°. Further crops were lower melting and oily. The total recrystallized yield of $C_6H_5HgCCl_2H$ totalled 5.3 g (71%).

Reaction with phenyl(dibromochloromethyl)mercury. To 0.019 mole of phenyl-(dibromochloromethyl)mercury in 185 ml of benzene and 40 ml of pentane cooled in an ice bath under nitrogen was added over a five-min period 0.022 mole of tri-n-butyltin hydride in 6 ml of benzene. The reaction mixture was stirred and allowed to come to room temperature. Addition of 60 ml of KF solution and 60 ml of acetone resulted in precipitation of 5.2 g (76%) of light gray, crude tri-n-butyltin fluoride. Evaporation of the organic layer at reduced pressure left a yellow oil as residue. Extraction of the latter with 100 ml of 4 : 1 pentane/chloroform and chilling of the extracts (following filtration from 0.4 g of white flakes) produced 1.4 g of off-white crystals, m.p. 58–62° (19% crude yield of $C_6H_5HgCBrClH$). The oily residue obtained upon concentration of the mother liquor could not be crystallized. A sample of the crude solid product was recrystallized twice from chloroform/hexane, yielding colorless needles, m.p. 65–67°.

Reaction with phenyl(tribromomethyl)mercury. To 0.018 mole of phenyl-(tribromomethyl)mercury in 130 ml of benzene and 40 ml of pentane cooled in an ice bath under nitrogen was added dropwise over a period of one hour 0.019 mole of tri-n-butyltin hydride in 5 ml of benzene. The mixture was stirred and allowed to warm slowly to room temperature. The reaction mixture was filtered from a small amount of mercury and then treated with 50 ml each of KF solution and anhydrous acetone. Four g (72%) of crude tri-n-butyltin fluoride precipitated. Evaporation of the dried organic layer at reduced pressure left a gray oil. This was extracted with 50 ml of chloroform. The extracts were filtered from 0.3 g of gray, flaky solid which appeared, and 70 ml of hexane was added. Chilling of the chloroform/hexane solution resulted in crystallization of 1.5 g of white solid, m.p. 62–70°, which represents a 19% crude yield of $C_6H_5HgCBr_2H$. Further crops consisted of phenylmercuric bromide, obtained as colorless flakes of m.p. 280–284°. A portion of the crude product was recrystallized from warm pentane to give colorless crystals, m.p. 62–66°. Further recrystallization from chloroform/hexane produced needles, m.p. 67–69°.

ACKNOWLEDGEMENTS

The authors are grateful to the U.S. Air Force Office of Scientific Research and the U.S. Army Research Office (Durham) for generous support of this work, and to M & T Chemicals, Inc. for gifts of bis(tri-n-butyltin) oxide. This investigation was supported in part by Public Health Service Fellowships 1-F1-GM-20,065-01 (to J.M.B.), 5-F1-GM-20,179-03 (to H.D.) and 1-F1-GM-25,063-01 (to H.D.S.).

SUMMARY

The reaction of phenyl(trihalomethyl)mercury compounds, $C_6H_5HgCX_2Br$ ($X = Cl$ and Br), with organosilicon and organogermanium hydrides in benzene at 80° results in insertion of CCl_2 and CBr_2, respectively, into the Si–H and Ge–H bonds to give Si–CX_2H and Ge–CX_2H compounds. Triethylgermane was found to be four times more reactive than triethylsilane, and triethylsilane was 0.8 times as reactive as cyclohexene. Evidence was obtained which suggests that dihalocarbenes (free or complexed) are involved as intermediates in these reactions. Tri-n-butyltin hydride reduced the C–Br bond of $C_6H_5HgCX_2Br$ mercurials, and $C_6H_5HgCCl_2H$, C_6H_5Hg·CClBrH and $C_6H_5HgCBr_2H$ were prepared and characterized. However, this is not a practical preparative route to these mercurials.

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