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A STUDY OF SOME ORGANOTRICHLOROGERMANES PREPARED FROM CESIUM TRICHLOROGERMANATE(II)*

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SUMMARY

The chemical reactions of cesium trichlorogermanate(II) to form $RGeCl_3$ compounds have been reexamined, the older methods improved upon, and new techniques put forth. In the course of these studies, tert-butyltrichlorogermane and sec-butyltrichlorogermane and their triphenyl derivatives were prepared and characterized by means of NMR and infrared spectral data, and elemental analyses. Mechanistic possibilities for the reactions involved were probed in the light of steric limitations set by the reactants, and the overriding nucleophilicity of the $GeCl_3^-$ group.

INTRODUCTION

The classical techniques[1] for the preparation of $RGeCl_3$ compounds (R = alkyl, aryl) have invariably led to the formation of mixed products of the type R_nGeCl_{4-n} ($n = 1, 2, 3$) and varying amounts of digermanes[2]. However, the formation of $RGeCl_3$ compounds in high yield by means of simple, catalyzed redistribution reactions was reported recently[1c].

It was the purpose of this paper to reinvestigate the chemical reactivity of $CsGeCl_3$[3], a substance which seemed to afford a direct route to organotrichlorogermanes:

$$CsGeCl_3 + RI \rightarrow RGeCl_3 + CsI$$

This reaction precludes the possibility of multiple products and is somewhat analogous to the reactions of trichlorogermane with tertiary alkyl chlorides[4] and with olefins[5]. More specifically, this paper deals with the preparation of new, relatively crowded butyltrichlorogermanes, and compares their unusual physical properties with those of analogous silicon compounds.

A reinvestigation of the general nature of the reactions of cesium trichlorogermanate(II)*** appeared to be in order. The original work was therefore extended

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*** It is assumed throughout that the valence state of germanium in the $CsGeCl_3$ salt is +2. Evidence derived from physical and chemical properties along with far infrared data[6] strongly suggest that the conclusions drawn are correct.

to include a solid–liquid phase "intimate mixture" technique, and a more conventional combination of reactants in stirred solutions of common organic solvents. Of special interest were the steric requirements set by the alkyl iodides on the course of the reaction and the overall nucleophilicity of the $Ge^{II}Cl_3^-$ anion in displacement type reactions.

EXPERIMENTAL

I. Preparation of $CsGeCl_3$

Cesium trichlorogermanate(II) was prepared in the manner described by Tchakirian[3]. To somewhat simplify the literature process, germanium tetrachloride was directly reduced to germanium(II) in aqueous hydrochloric acid.

In a typical experiment, 70 g of hypophosphorous acid (0.53 moles or slightly more than a four to one excess) and 80 ml of 3 *M* hydrochloric acid were warmed in a 1000 ml beaker equipped with a watch glass and magnetic stirrer. Germanium tetrachloride (28.19 g, 0.131 moles) was added and the temperature raised to 85–90°. The solution was vigorously mixed for 5 h, then cooled to 50°. The addition of a 5% molar excess of solid cesium chloride produced a fluffy white precipitate upon further cooling to room temperature. The solid (34.40 g, 84%) was filtered and dried at 25° for 8 h. (Found: Cl. 33.97. $CsGeCl_3$ calcd.: Cl, 34.09%.) All analyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

II. Sealed tube reactions of $CsGeCl_3$

In place of standard Carius tubes, 10 mm o.d. glass break-seal tubes (purchased from Scientific Glass Apparatus) were employed as reaction vessels. After

TABLE 1

REACTIONS OF $CsGeCl_3$

No.	Reaction	Conditions	Product[a]	Yield	Properties
Sealed tube reactions					
1	$CsGeCl_3 + C_6H_5I$	200°, 38 h	$C_6H_5GeCl_3$	50%	
2	$CsGeCl_3 + tert\text{-}C_4H_9I$	140°, 840 h	$tert\text{-}C_4H_9GeCl_3$	40%	m.p. 66–67° (subl.)
3	$C_6H_5Li + tert\text{-}C_4H_9GeCl_3$	50–60°, 7 h	$tert\text{-}C_4H_9Ge(C_6H_5)_3$		m.p. 160–62°
Solid–liquid phase reactions					
4	$CsGeCl_3 + n\text{-}C_4H_9I$	160°, 216 h	$n\text{-}C_4H_9GeCl_3$	70%	b.p. 183–87°
5	$CsGeCl_3 + sec\text{-}C_4H_9I$	140°, 240 h	$sec\text{-}C_4H_9GeCl_3$	26%	b.p. 184–85°
6	$C_6H_5Li + sec\text{-}C_4H_9GeCl_3$	50–60°, 5 h	$sec\text{-}C_4H_9Ge(C_6H_5)_3$		m.p. 70–71°
7	$CsGeCl_3 + CH_2{=}CHCH_2I$	120°, 36 h	$CH_2{=}CHCH_2GeCl_3$	60%	b.p. 154–57°
8	$C_6H_5Li + CH_2{=}CHCH_2GeCl_3$	50–60°, 5 h	$CH_2{=}CHCH_2Ge(C_6H_5)_3$		m.p. 87–89°
9	$CsGeCl_3 + iso\text{-}C_3H_7I$	120°, 96 h	$iso\text{-}C_3H_7GeCl_3$	4%	
Solution reactions					
10	$CsGeCl_3 + CH_3I$	Reflux 17 h in THF	CH_3GeCl_3	47%	b.p. 108°
11	$CsGeCl_3 + C_6H_5CH_2Cl$	Reflux 14 h in methanol	$C_6H_5CH_2GeCl_3$	30%	m.p. 33–36°

[a] *Analyses*: tert-BuGePh$_3$ (Found: C, 73.13; H, 6.66. $C_{22}H_{24}Ge$ calcd.: C, 73.19; H, 6.70%); sec-BuGePh$_3$ (Found: C, 73.31; H, 6.90. $C_{22}H_{24}Ge$ calcd.: C, 73.19; H, 6.70%); $CH_2{=}CHCH_2GeCl_3$ (Found: C, 16.16; H, 2.24. $C_3H_5Cl_3Ge$ calcd.: C, 16.38; H, 2.29%).

addition of solid $CsGeCl_3$ and about a 25% molar excess of reactant iodide, the tubes were evacuated at liquid nitrogen temperature before sealing, then heated in an electric oven. When the reaction was completed, the break-seal apparatus was attached to a high-vacuum line and refrozen before opening. The contents were then directly distilled through traps set at zero and −196° respectively.

In reactions 1 and 2 (Table 1), $RGeCl_3$ products were collected essentially free of reactants in the 0° trap, and were subsequently analyzed.

Triphenyl derivatives were prepared by addition of excess phenyllithium (purchased from Foote Mineral, 2 *M* in 70/30 benzene/ether) to the $RGeCl_3$ species. Upon hydrolysis, separation, and solvent evaporation, white crystals were obtained and recrystallized from absolute methanol. Table 1 outlines details of reactions, physical properties, yields, and analyses.

III. Solid–liquid phase reactions of $CsGeCl_3$

An experimental procedure somewhat similar to that used by Lesbre[7] in reactions of $CsPbCl_3$ was employed to prepare some alkyltrichlorogermanium compounds. Alkyl iodides (25% molar excess) were refluxed over solid cesium trichlorogermanate(II) under a slight positive pressure of nitrogen. An oil bath was used to maintain a temperature approximately 20° above the boiling point of iodide to support a gentle reflux. When the reaction was completed, products were directly distilled from the intimate mixture apparatus, purified, and characterized (Table 1). Triphenyl derivatives were prepared as above.

IV. Solution reactions of $CsGeCl_3$

In a typical experiment, $CsGeCl_3$ (0.042 moles) and methyl iodide (0.168 moles) were added with 500 ml of dry tetrahydrofuran (THF) to a 1000-ml round-bottom flask equipped with a reflux column and calcium chloride drying tube. After 17 h of reflux, the more volatile products and solvent THF were distilled off, the major portion boiling at 67–68°, the final fraction boiling at 107.5–108°. Methyltrichlorogermane boils[1] at 111°. NMR and infrared spectra confirm the presence of CH_3GeCl_3 (4.3 g, 47%). Benzyltrichlorogermane was similarly prepared in methanol solvent (Table 1).

V. Infrared and nuclear magnetic resonance spectra

Table 2 groups the $GeCl_3$, Ge–C, and phenyl–germanium frequencies for eleven organogermanium compounds. Although it is difficult to make generalizations about the position of the Ge–C stretch, agreement is good with the literature data[8,9], the region of this characteristic band[12] being at 520–600 cm^{-1}. The position of the asymmetric Ge–Cl stretch is invariant in the $RGeCl_3$ compounds studied at 426–430 cm^{-1}. These latter bands are intense and sharp in all cases. In addition to Whiffen's[13] diagnostic narrow phenyl–germanium regions at 1430 and 1090 cm^{-1}, there appears to be another characteristic absorption area between 460 and 470 cm^{-1}.

Of some interest are the near infrared C–H stretches of tert-butylorganogermanes. Complex multiplets of five, medium intensity, sharp absorption bands are noted from 2860 through 2975 cm^{-1}. The tert-butyl skeletal vibrations occur at 940–950 cm^{-1} (weak), 1014–1020 cm^{-1} (medium), and 1170–1190 cm^{-1} (medium). Characteristic C–H deformation bands are observed at 1461 and 1470 cm^{-1} in the

TABLE 2

CHARACTERISTIC INFRARED VIBRATIONAL FREQUENCIES[a] OF ORGANOTRICHLOROGERMANES AND ORGANOTRIPHENYLGERMANES

Compound	Ge–Cl	Ge–C	Ge–C_6H_5		
CH_3GeCl_3	426	631			
iso-$C_3H_7GeCl_3$	429	575			
n-$C_4H_9GeCl_3$	428	593			
sec-$C_4H_9GeCl_3$[b]	429	560, 583			
tert-$C_4H_9GeCl_3$	427	550			
$H_2C{=}CHCH_2GeCl_3$	429	548			
$C_6H_5CH_2GeCl_3$	430	558			
$C_6H_5GeCl_3$	430	610	457	1090	1438
$H_2C{=}CHCH_2Ge(C_6H_5)_3$		534	465	1094	1436
tert-$C_4H_9Ge(C_6H_5)_3$		541	471	1089	1431
sec-$C_4H_9Ge(C_6H_5)_3$[b]		540, 572	469	1091	1432

[a] All spectra were run on a Beckman I.R. 9 Recording Spectrophotometer, either as liquid films, or Nujol mulls between 6 mm KBr windows. Vibrational frequencies are listed in wave numbers (cm^{-1}). [b] For the sec-butyl compounds, the two Ge–C vibrations probably correspond to an asymmetric stretch (583, 572 cm^{-1}) and a symmetric stretch (560, 540 cm^{-1})[11]. In most cases, only one band is observed.

form of a medium doublet.

Pertinent features for the trichloro- and triphenylallylgermanium compounds are listed in Table 3. The assignments agree well with the figures reported by Chumaevskii[8].

TABLE 3

PERTINENT INFRARED ABSORPTIONS OF TWO ALLYLGERMANIUM COMPOUNDS

$Cl_3GeCH_2CH{=}CH_2$	$(C_6H_5)_3GeCH_2CH{=}CH_2$	Assignment
429(s)		Ge–Cl stretch
548(w)	534(w)	Ge–C stretch
1165, 1186(w)	1188(w)	Allylic C–H bands
1637(m)	1632(m)	Allylic C=C stretch
3092(m)	3073(m)	Terminal H–C= stretch

Table 4 lists nuclear magnetic resonance data confirming structures of seven organotrichlorogermanium compounds prepared above.

RESULTS AND DISCUSSION

The organotrichlorogermanes described herein are either high-boiling liquids or volatile solids. All $RGeCl_3$ species are readily hydrolyzed by moist air or water to the corresponding solid oxide form $(RGeO)_2O$*.

Table 5 records boiling and melting points of the butyltrichloro isomers of germanium and silicon. One observes a nearly invariant list of boiling points for all the butyl compounds of a particular Group IV metal except in the case of tert-butyl-

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* The starting material $CsGeCl_3$ is initially hydrolyzed to $Ge(OH)_2$, loses water to form GeO, and is eventually oxidized to the stable GeO_2 form[3].

TABLE 4

NMR SPECTRAL DATA FOR SOME ORGANOTRICHLOROGERMANES

Compound	Chemical shift[a]		Integration
	CH_2, CH_3	C_6H_5	ratios
CH_3GeCl_3	1.77[b] (singlet)		
tert-$C_4H_9GeCl_3$	1.42 (singlet)		
$C_6H_5GeCl_3$		7.10, 7.23	3:2[c]
$C_6H_5CH_2GeCl_3$	3.43 (singlet)	7.43 (singlet)	2:5
n-$C_4H_9GeCl_3$	1.1, 1.75, 2.15		3:4:2[d]
sec-$C_4H_9GeCl_3$	1.4, 2.0		8:1[e]
iso-$C_3H_7GeCl_3$	1.37, 2.24		6:1[f]

[a] Parts per million from tetramethylsilane; multiplets unless stated otherwise. [b] Lit. 10: 1.83 ppm. [c] Ratio of *meta, para* to *ortho* H's. [d] Ratio of three terminal H's to two H's on the carbon atom α to the $GeCl_3$ group. [e] Ratio of one tertiary H to eight primary and secondary H's. [f] Ratio of one tertiary H to six methyl H's.

trichlorogermane. Both tert-$C_4H_9GeCl_3$ and tert-$C_4H_9SiCl_3$ are white, sublimable solids at room temperature and atmospheric pressure. In addition, tert-butyltrichlorosilane exists in the form of "well defined fern-like crystals"[14]. The same phenomenon has now been observed in the case of the germanium analog, as well as for tetrakis(trimethylsilyl)silane[15]. The effect of symmetric branching on the physical state and melting point of molecules has elicited a good deal of interpretation and discussion[16]. Apparently, the three compounds listed above have the correct symmetry to fit rather tightly into compact crystalline lattices, thus maximizing intermolecular forces and producing volatile solids.

The reaction of $CsGeCl_3$ with alkyl iodides to produce organotrichlorogermanes was first studied by Tchakirian[3]. Whereas it appeared necessary to employ drastic conditions of heated, sealed Carius tubes to make the reaction feasible, it was thought that less severe methods should be investigated in light of the ease of preparation and good stability of the cesium trichlorogermanate(II) starting material. To that end, work was done with solid–liquid phase reactions, and a preliminary attempt at solution reactions of $CsGeCl_3$ was carried out. The former empirical technique provided not only a somewhat general method for producing primary and some secondary alkyltrichlorogermanes, but also added insight into the nature of the reactive process.

Yields of $RGeCl_3$ products reflected the degree of steric interference at the site

TABLE 5

BOILING AND MELTING POINTS OF THE ISOMERS OF BUTYLTRICHLOROGERMANE AND BUTYLTRICHLOROSILANE

$RGeCl_3$[a]	B.p. [°C(mm)]	M.p. (°C)	$RSiCl_3$[b]	B.p. [°C(mm)]	M.p. (°C)
n-C_4H_9–	184° (760)		n-C_4H_9–	148.8° (760)	
sec-C_4H_9–	184° (752)		sec-C_4H_9–	144° (760)	
tert-C_4H_9–	92.5° (68)	66–67°[c]	tert-C_4H_9–	133° (740)	98–99°
iso-C_4H_9–	108° (25)		iso-C_4H_9–	139.5° (745)	

[a] For germanium compounds not described above see ref. 1. [b] For silicon compounds see ref. 17. [c] Mironov and Gar[4] list a (apparently sealed tube) melting point of 95–98°.

of attachment of the iodine atom in the alkyl iodide reactants (Reactions 4, 5, 7, 9; Table 1). Both allyl and n-butyl iodides produced yields in excess of 60%. The crowded sec-butyl iodide gave a 26% yield of $RGeCl_3$; isopropyl iodide only 4%.

It is interesting to note that in solution, the reactivity of $GeCl_3^-$, as derived from $CsGeCl_3$, seems to be enhanced to some degree. Solvent assistance by either tetrahydrofuran or methanol could be taking place to solvate the cesium cation, thereby activating the trichlorogermanate(II) anion. Thus the relatively high yields of CH_3GeCl_3 (47%) and $C_6H_5CH_2GeCl_3$ (30%) noted above could be explained (Reactions 10 and 11).

A simple assignment of oxidation states in these reactions shows that a formal oxidation of germanium from +2 in $CsGeCl_3$ to +4 in $RGeCl_3$ is taking place. An expected driving force, the formation of a stable germanium(IV) entity, is apparently partially negated by a nearly equal force to retain the stable $CsGeCl_3$ species in preference to the product CsI. This latter postulate might take some precedence from the fact that the relatively "hard" Cs^+ ion would be expected to prefer the relatively hard $GeCl_3^-$ anion over the "soft" iodide anion.

A more complex situation seems to exist in reactions of $SnCl_3^-$ (ref. 18) and $PbCl_3^-$ (ref. 7) with alkyl iodides. The authors report that isopropyl iodide reacts more easily than n-propyl iodide. Furthermore, the products are respectively iso-propyltrichlorostannane and n-propyltriiodostannane. Similar iodine–chlorine exchanges have never been observed in the corresponding germanium cases.

Another steric problem was encountered in the course of the present study. The reaction to produce tert-butyltriphenylgermane proceeded in a straightforward manner, apparently uncomplicated by the coupling mechanism[2] by which digermanes

$$\text{tert-}C_4H_9GeCl_3 + 3\ C_6H_5Li \rightarrow \text{tert-}C_4H_9Ge(C_6H_5)_3 + 3\ LiCl$$

are formed in similar cases.

$$GeCl_4 + \text{excess } C_6H_5Li \rightarrow Ge(C_6H_5)_4 + (C_6H_5)_3Ge{-}Ge(C_6H_5)_3$$

The fact that three phenyl groups were substituted with relative ease is a little surprising when the precursor to the triphenyl compound, $(\text{tert-}C_4H_9)Ge(C_6H_5)_2Cl$, appears to be quite sterically hindered from further nucleophilic attack. The melting point of the new compound tert-butyltriphenylgermane is relatively high (160–162°) and no sign of sublimation was observed. Similarly, the ready formation of sec-butyltriphenylgermane through the crowded intermediate $\text{sec-}C_4H_9Ge(C_6H_5)_2Cl$ occurs without any hint of coupled product. It might be postulated that the large, branched, three-dimensional butyl groups are impeding a lithium transfer process no doubt responsible for digermane formation. The flat, two-dimensional phenyl rings could then be said to be incapable of such steric blocking.

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