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Generation of Germyl, Stannyl, and Plumbyl Anions through Nucleophilic Cleavage of Digermanes, Distannanes, and Diplumbanes

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ABSTRACT

Nucleophilic cleavage by potassium t-butoxide on hexaphenyl digermanes, distannanes, and diplumbanes, in N,N'-dimethylpropyleneurea (DMPU) solvent, provides a facile method for preparation of triphenyl germyl, stannyl, and plumbyl anions.

INTRODUCTION

In previous articles in this series, we have probed different aspects of the electronic configurations of phenyl substituted group 4 anion-alkali metal compounds [1]. Of interest is evaluation of the importance of charge delocalization vs. π-polarization in the anions as the group 4 element is changed from carbon to silicon, germanium, tin, and lead: the nature of the group 4 element–alkali metal bond; and the influence of solvent medium on these characteristics. Another goal of these studies is to gain insight on the relative stabilities of the anions as one proceeds down the group 4 family of elements.

It was of interest, therefore, to explore different methods of preparation of these anions, especially if such methods could give insight on relative stabilities. Commonly used methods [2–4], such as reaction of alkali metals with the group 4 element halides, R_3EHal, hydrides, R_3EH, or hexaorgano derivatives, R_3EER_3, have limitations in providing fundamental information of this type.

We have recently reported that nucleophilic cleavage by potassium *tert*-butoxide, of disilanes, $R_3SiSiR'_3$, where R,R' is methyl or phenyl, affords a facile method for the preparation of silyl anions [5]. As well, the direction of cleavage, i.e., generation of R_3SiK or R'_3SiK, could yield information on relative stabilities of the respective anions. In the present work, we explore this method toward the preparation of germyl, stannyl, and plumbyl anions.

RESULTS AND DISCUSSION

We have found that triphenyl germyl, stannyl, and plumbyl anions can readily be formed by nucleophilic cleavage of the hexaphenyl digermanes, distannanes, and diplumbanes with potassium *t*-butoxide according to Equations 1–3:

$$Ph_3GeGePh_3 + Me_3COK \rightarrow Ph_3GeK + Ph_3GeOCMe_3 \quad (1)$$

$$Ph_3SnSnPh_3 + Me_3COK \rightarrow Ph_3SnK + Ph_3SnOCMe_3 \quad (2)$$

$$Ph_3PbPbPh_3 + Me_3COK \rightarrow Ph_3PbK + Ph_3PbOCMe_3 \quad (3)$$

The reactions, when conducted in *N,N'*-dimethylpropyleneurea (DMPU) at 0°C, gave a reasonable yield of the anions (Table 1), as shown by the ^{13}C NMR spectra. The ^{13}C NMR spectral characteristics of the triphenyl germyl, stannyl, and plumbyl anions as obtained in this work are given in Table 2. A representative ^{13}C NMR spectrum

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Dedicated to Prof. Adrian Gibbs Brook on the occasion of his seventieth birthday.

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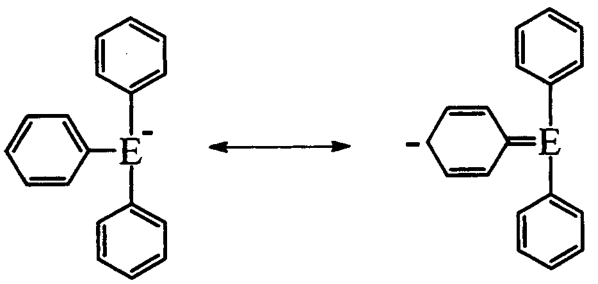
TABLE 1 Generation of Germyl, Stannyl, and Plumbyl Potassium Compounds (R_3EK) through Nucleophilic Cleavage of Digermanes, Distannanes, and Diplumbanes (R_3EER_3) with Potassium *t*-Butoxide

R_3EER_3	*Solvent*	*Temperature (°C)*	*Time (h)*	*R_3EK*	*Yield (%)*
$Ph_3GeGePh_3$	DMPU	0	24	Ph_3GeK	60
$Ph_3SnSnPh_3$	DMPU	0	0.5	Ph_3SnK	85
$Ph_3PbPbPh_3$	DMPU	0	0.5	Ph_3PbK	90

showing the products of reaction of $Ph_3SnSnPh_3$ with *t*-BuOK is presented in Figure 1.

In contrast to the applicability of DMPU as the solvent, attempted use of tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) gave no yield of the anions under corresponding conditions. It is interesting that, in the preparation of the silyl anions from disilanes, THF and DME were suitable solvents but DMPU was not. This may be related to the formation of contact vs. solvent separated ion pairs [1,6–8] and different stabilities of these species as the group 4 element is changed. The group 4 anions of higher atomic number investigated in this work are expected to exist as the solvent separated ion pairs in the relatively polar solvent, DMPU. The requirement for more effective solvation of anions thus appears to be a critical factor in Reactions 1–3.

We have previously [1,9,10] addressed the question of the importance of charge delocalization in group 4 anions, i.e.,



While for the triphenylmethyl anion (E = C) this type of delocalization is well established, it remained an open question to what extent, if any, this operates for the corresponding germyl, plumbyl, and stannyl anions. The results argue conclusively against this type of delocalization for E = Ge, Sn, and Pb. Figure 2 shows the expected charge distribution in the anions by the resonance mechanism (R_π) and caused by a π-inductive effect or π-polarization (F_π). The results expressed in the form $\Delta\delta$ (CK-CCl) and $\Delta\delta$ (SnK-SnCl) in parts per million show the contrast in the two systems. For $Ph_3C^-K^+$, the observed charge distribution pattern corresponds to delocalization by resonance, while in $Ph_3Sn^-K^+$, π-polarization is seen to be operative.

TABLE 2 ^{13}C NMR Chemical Shifts of Group 4 Anions (δ, ppm)[a],[b]

	C-1	*C-2*	*C-3*	*C-4*
Ph_3GeK	166.3	137.3	126.6	123.5
Ph_3SnK	167.7	139.2	126.9	124.3
Ph_3PbK	191.1	140.2	128.1	123.7

[a] 0.1M solutions in DMPU solvent.

[b] Cyclohexane used as an internal reference at 27.7 ppm; Bruker 400 MHz instrument.

CONCLUSIONS

Our work has demonstrated the feasibility of preparation of the group 4 anions Ph_3E^- (E = Si, Ge, Sn, Pb) through nucleophilic cleavage of Ph_3EEPh_3 by *t*-butoxide. Choice of solvent is important for success in the preparations. Extension of the studies to unsymmetrical species, $R_3EER'_3$ and $R_3EE'R_3$, would provide information on relative stabilities of group 4 anions as the substituent and the group 4 element are varied. ^{13}C NMR characteristics of the anions provide information on charge distribution and transmission of electronic effects, resonance vs. π-polarization.

EXPERIMENTAL SECTION

Materials and Procedures

1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidone (DMPU) and cyclohexane were purchased from Fluka, and potassium *t*-butoxide was procured from Alfa. The cyclohexane was treated with sodium wire overnight and then distilled under argon into a vessel containing freshly cut shiny potassium metal and distilled again under argon. The distillation from potassium metal was repeated once more, and the final distillate was kept over sodium wire in a septum sealed flask from which solvent was transferred by syringe under argon. The DMPU was allowed to stand over molecular sieves (4A grade) overnight and filtered in an argon flushed glove box. This treatment was repeated three times, and the resulting solvent was stored under argon over molecular sieves. Potassium *t*-butoxide was purified by sublimation under vacuum at 150–160°. A solution of ^tBuOK in DMPU prepared under argon, when kept in the refrigerator, remained colorless for several days after which it was not used in the preparations.

The apparatus used in the work was described previously [9]. In a typical preparation, the sublimed ^tBuOK (1.8 g) was introduced into a 50 mL round bottom flask under argon in a glove box, solvent (20 mL) was added, and the flask was septum-capped, removed from the glove box, and stirred magnetically to yield a clear solution. The

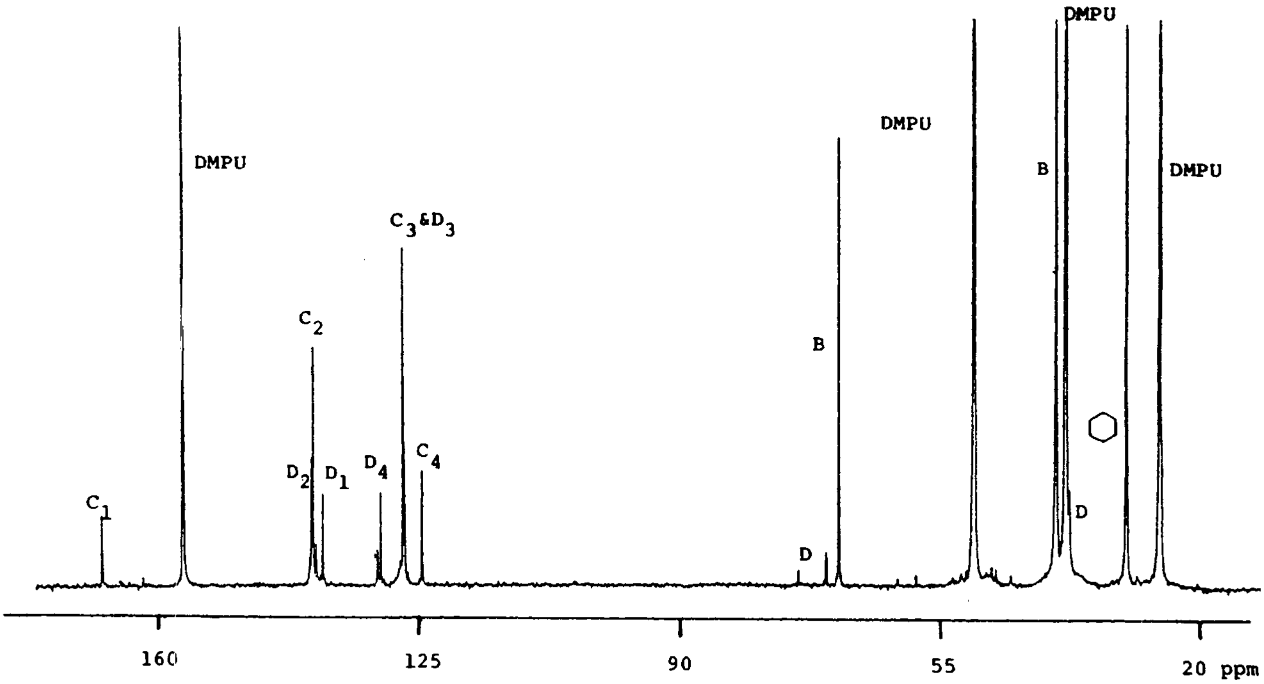


FIGURE 1 ^{13}C NMR spectrum of products of reaction between $Ph_3SnSnPh_3$ and potassium *t*-butoxide in DMPU at 0°C after 30 min. The peaks are designated as (A) $Ph_3SnSnPh_3$, (B) $(CH_3)_3COK$, (C) Ph_3SnK, and (D) $Ph_3SnOCMe_3$. The subscripts 1, 2, 3, and 4 refer to *ipso*, *ortho*, *meta*, and *para* carbons, respectively. Cyclohexane was used as an internal reference (27.7 ppm).

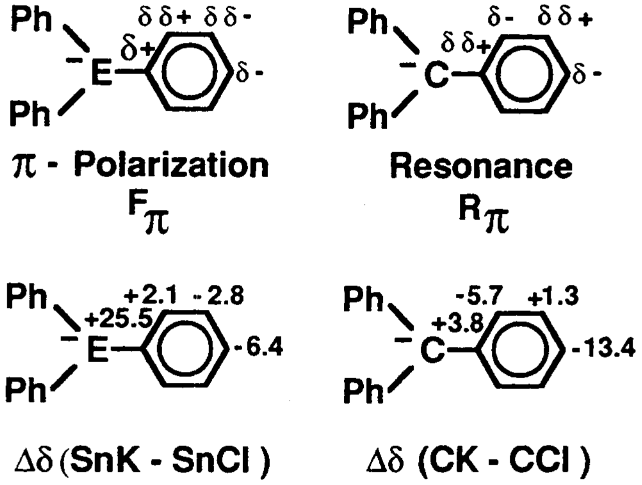


FIGURE 2 ^{13}C chemical shift changes on going from triphenyl chloride derivatives to the corresponding potassium salts, and expected charge distributions in the anions by π-polarization (F_π) and resonance (R_π).

^{t}BuOK solution (5 mL) was added by means of a syringe to a septum-capped 20 mL tube containing 0.1 g of substrate, and the reaction was allowed to occur at various temperatures and reaction times. The extent of the reaction was followed by transferring an aliquot of the reaction solution by syringe under argon into a septum-capped NMR tube, adding cyclohexane as an internal reference, and recording the NMR spectrum.

NMR spectra were recorded on a Bruker 400 MHz multinuclear spectrometer with selective decoupling. The spectrometer was standardized by means of ethylbenzene.

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