

## NOTE

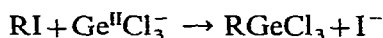
## REACTIONS OF TRICHLOROGERMANATE(II) SALTS WITH AROMATIC SUBSTRATES\*

PAUL S. POSKOZIM\*\* AND AUBREY L. STONE

*Department of Chemistry, Sam Houston State College, Huntsville, Texas 77340 (U.S.A.)*

(Received November 5th, 1968)

The reaction of trichlorogermanate(II) salts with organic halides is generally thought to involve a nucleophilic attack by a  $\text{GeCl}_3^-$  anion<sup>1</sup>. However, due to the



general insolubility of the  $\text{MGeCl}_3$  salts<sup>2</sup> ( $\text{M} = \text{Cs}^+, \text{Rb}^+$ ) and the solvent free conditions of the intimate mixture and sealed tube reactions used herein, it might be difficult to think of a mobile, nucleophilic  $\text{GeCl}_3^-$  species.

It was thought that the reaction of  $\text{GeCl}_3^-$  with  $\text{PhCH}_2\text{CH}_2\text{I}$  could shed some light on the mechanistic pathway employed in these cases. In a purely qualitative sense, if the reaction proceeded in any way other than a simple nucleophilic displacement, namely via an ionic or concerted process, there appeared likelihood of some rearrangement. Specifically, a carbonium ion mechanism might lead to  $\text{PhCH}(\text{GeCl}_3)\text{CH}_3$  through the stabilized benzyl cation  $\text{PhCH}^+\text{CH}_3$ .

Nuclear magnetic resonance spectral data from the initial reaction of (2-

TABLE I

REACTIONS OF TRICHLOROGERMANATE(II) SALTS

Reactants	Conditions	Organogermanium product	Yield (%)
(1) $\text{Ph}(\text{CH}_2)_2\text{I}/\text{Me}_3\text{NHGeCl}_3$	Intimate mixt., 5 days, 175°	$\text{Ph}(\text{CH}_2)_2\text{GeCl}_3$	90
(2) $\text{Ph}(\text{CH}_2)_2\text{I}/\text{Me}_3\text{NHGeCl}_3$	Sealed tube, 2 days, 200°	$\text{Ph}(\text{CH}_2)_2\text{GeCl}_3$	15
(3) $\text{Ph}(\text{CH}_2)_2\text{I}/\text{Me}_3\text{NHGeCl}_3$	Reflux 96 h, tetrahydrofuran	$\text{Ph}(\text{CH}_2)_2\text{GeCl}_3$	26
(4) $\text{Ph}(\text{CH}_2)_2\text{I}/\text{Me}_3\text{NHGeCl}_3$	100–105°, 36 h, nitrobenzene		
(5) $\text{PhCH}(\text{Br})\text{CH}_3/\text{CsGeCl}_3$	Intimate mixt., 5 days, 160°	$\text{PhCH}(\text{GeCl}_3)\text{CH}_3$	89

\* Based in part on the M. A. Thesis of Aubrey L. Stone, Sam Houston State College, 1968.

\*\* Present address: Department of Chemistry, Northeastern Illinois State College, Chicago, Illinois 60625.

iodoethyl)benzene with trimethylammonium trichlorogermanate(II) [intimate mixture procedure, Table 1, reaction (1)] indicated the presence of what was at first thought to be a rearranged product [1-(trichlorogermylethyl)benzene]. A complete gas chromatographic analysis of the reaction mixture, however, identified an elimination product, styrene, in addition to unreacted iodide and product [2-(trichlorogermylethyl)benzene] in about a 1/1/90 ratio. The previously unreported compounds [1-(trichlorogermylethyl)benzene and the phenyl derivative [1-(triphenylgermyl)ethyl]benzene were subsequently directly prepared and unambiguously identified.

It was not possible to induce a rearrangement in the  $\text{PhCH}_2\text{CH}_2\text{I}$  system in tetrahydrofuran (THF) or nitrobenzene solvents (Table 1). In the former, the yield of product  $\text{PhCH}_2\text{CH}_2\text{GeCl}_3$  was 26% while in the latter, elimination of HI successfully competed with reaction with  $\text{Me}_3\text{NHGeCl}_3$ , and styrene was the only identifiable product in the gas chromatogram. Likewise, the sealed tube technique had an inhibiting influence on the course of the reaction.

Although kinetic data are not available, results here, consistent with previous work<sup>1</sup>, seem to rule out carbonium ion mechanisms from reactions involving  $\text{GeCl}_3^-$  salts. It is interesting to note that the trimethylammonium salt  $\text{Me}_3\text{NHGeCl}_3$  seems to be at least as reactive as the cesium salt, and is, in addition, significantly more soluble in organic solvents such as THF, nitrobenzene, and benzene.

#### EXPERIMENTAL

The sealed tube reaction was carried out in a Fisher and Porter Combustion Tube (Model 320-002). The intimate mixture technique and preparation of  $\text{CsGeCl}_3$  have been previously described<sup>1</sup>. Trimethylammonium trichlorogermanate(II) was similarly prepared from germanium tetrachloride reduced with hypophosphorous acid in a 3 M hydrochloric acid solution upon addition of  $\text{Me}_3\text{NHCl}$ . Melting point of  $\text{Me}_3\text{NHGeCl}_3$ : 189–191°. (Found: C, 14.63; H, 4.48; N, 5.42.  $\text{C}_3\text{H}_{10}\text{Cl}_3\text{GeN}$  calcd.: C, 15.07; H, 4.20; N, 5.86%.)

$\text{PhCH}_2\text{CH}_2\text{I}$  and  $\text{PhCH}(\text{Br})\text{CH}_3$  were purchased from Eastman Organic

TABLE 2

PHYSICAL PROPERTIES AND ANALYSES OF ORGANOGERMANIUM PRODUCTS

Compound	B.p. [°C(mm)]	M.p. (°C)	Infrared data ( $\text{cm}^{-1}$ )			Analyses (%)	
			$\nu(\text{Ge}-\text{C})$	$\nu(\text{Ge}-\text{Cl})$	$\nu(\text{Ge}-\text{Ph})$	Calcd.	Found
$\text{PhCH}(\text{GeCl}_3)\text{CH}_3$	277–278		552	425		C, 33.80 H, 3.17	34.58 32.29
$\text{PhCH}_2\text{CH}_2\text{GeCl}_3$	132(10) <sup>b</sup>		545	415		C, 33.80 H, 3.17	39.94 3.52
$\text{PhCH}(\text{GePh}_3)\text{CH}_3$		114–116	568		464, 1090, 1428	C, 76.46 H, 5.88	76.67 5.92
$\text{PhCH}_2\text{CH}_2\text{GePh}_3$		144–145 <sup>a</sup>	549		467, 1090, 1430	C, 76.46 H, 5.88	76.96 5.96

<sup>a</sup> Reported<sup>4</sup>: m.p. 145–146°. <sup>b</sup> Ref. 3.

Chemicals and used without further purification. Table 1 lists reactants, conditions, organogermanium products, and yields. [1-(Trichlorogermyl)ethyl]benzene and [2-(trichlorogermyl)ethyl]benzene are high boiling liquids, easily separated from the intimate mixture apparatus by extraction with petroleum ether.

The triphenyl derivatives [1-(triphenylgermyl)ethyl]benzene and [2-(triphenylgermyl)ethyl]benzene were prepared from the corresponding chlorogermanes by the action of excess phenyllithium (Alfa Inorganics, Inc., 2.11 M in benzene/ether solution). Table 2 lists pertinent physical properties and analyses of the four organogermanium compounds prepared herein.

#### ACKNOWLEDGEMENT

The authors wish to cite the Office of Research and Grants of the Organized Research Program of Sam Houston State College for support for this work.

#### REFERENCES

- 1 P. S. POSKOZIM, *J. Organometal. Chem.*, 12 (1968) 115.
- 2 A. TCHAKIRIAN, *Ann. Chim.*, 12 (1939) 415.
- 3 N. G. DZHURINSKAYA, V. F. MIRONOV AND A. D. PETROV, *Dokl. Akad. Nauk SSSR*, 138 (1961) 1107.
- 4 M. C. HENRY AND M. F. DOWNEY, *J. Org. Chem.*, 26 (1961) 2299.

*J. Organometal. Chem.*, 16 (1969) 314-316