Organogermanium compounds

VI.[1] The preparation of some substituted (phenylethynyl)-trialkyl-germanes and -silanes

We have prepared by three methods substituted (phenylethynyl)triethylgermanes and -trimethylsilanes $X-C_6H_4-C{\equiv}C-MR_3$ required for kinetic studies. The first method, used for compounds having $X = H$ or p-Me, involved cross-metallation of the arylacetylene, $X-C_6H_4-C{\equiv}CH$, with n-butyl- or phenyllithium in ether followed by addition of chlorotrimethylsilane or bromotriethylgermane; the physical constants of the compounds thus prepared are shown in Table 1. The second method used for a range of alkyl-, methoxyl-, trifluoromethyl-, and halogen-substituted phenylethynyl compounds, involved treatment of the arylacetylene with ethylmagnesium bromide in tetrahydrofuran followed by addition of chlorotrimethylsilane or bromotriethylgermane. The physical constants of compounds thus obtained are given in Table 2. Contrary to a previous report[3], the Grignard reagents $X-C_6H_4-C{\equiv}C-MgBr$ react readily with bromotriethylgermane in tetrahydrofuran.

The third, novel, method was used to prepare phenyl- and p-tolylethynyltrimethylsilane; it involved treatment of phenyl- or p-tolylacetylene with chlorotrimethylsilane and sodium in boiling toluene.

Experimental

Preparations involving organolithium reagents. Phenyl- or n-butyllithium (0.10 mole, by titration) in ether (*ca.* 100 ml) was added to a stirred solution of the arylacetylene (0.10 mole) in ether (150 ml), and the mixture was then refluxed for 15 min. Chlorotrimethylsilane (0.12 mole) or bromotriethylgermane (0.12 mole) in ether (20 ml) was then added, and the mixture was refluxed for 1 h and then set aside overnight. Addition of saturated aqueous ammonium chloride, followed by separation, drying (Na_2SO_4), and fractionation of the ethereal layer gave the $X-C_6H_4-C{\equiv}C-MR_3$ compound having the properties listed in Table 1.

Preparations involving Grignard reagents. In a typical preparation, bromotriethylgermane (0.025 mole) in tetrahydrofuran (15 ml) was added to p-methoxyphenylethynylmagnesium bromide prepared by treatment of p-methoxyphenylacetylene (0.025 mole) with ethylmagnesium bromide (0.025 mole) in tetrahydrofuran (*ca.* 25 ml). The mixture was refluxed for 10 min, then cooled and treated with saturated aqueous ammonium chloride. Working up, as above, gave triethyl-(p-methoxyphenylethynyl)germane (90 %), with properties shown in Table 2.

Table 2 also lists the properties of other new $X-C_6H_4-C{\equiv}C-MR_3$ compounds, and of (2,3-dimethyl- and (2,4,6-trimethyl-phenylethynyl)triethylgermanes, prepared by this method.

TABLE 1

$X{-}C_6H_4{-}C{\equiv}C{-}MR_3$ COMPOUNDS MADE FROM ORGANOLITHIUM REAGENTS

MR$_3$	*X*	*b.p.* °/*mm*	n_D^{25}	*Yield*	*Found* (%)		*Required* (%)	
				(%)	*C*	*H*	*C*	*H*
$SiMe_3$[a]	H[b]	214/760	1.5262	80	—	—	—	—
$SiMe_3$	*p*-Me[c]	115/15.5	1.5328	85	76.9	8.9	76.5	8.6
$GeEt_3$	H[b]	115/1.5	1.5360	92	64.7	7.8	64.5	7.7
$GeEt_3$	*p*-Me[c]	147/5.8	1.5375	84	65.9	8.4	65.5	8.1

[a] Lit.², b.p. 87.5°/9 mm, n_D^{20} 1.5284.
[b] PhLi used for metallation.
[c] *n*-BuLi used for metallation.

TABLE 2

TRIALKYL(ARYLETHYNYL)GERMANES AND -SILANES, $X{-}C_6H_4{-}C{\equiv}C{-}MR_3$, PREPARED BY USE OF GRIGNARD REAGENTS

X	*b.p.* °/*mm*	n_D^{25}	*Yield*	*Found* (%)		*Required* (%)	
			(%)	*C*	*H*	*C*	*H*
MR_3 = $SiMe_3$							
o-Me	74/2.2	1.5218	74	76.4	8.4	76.5	8.6
p-OMe	96/1.5	1.5448	68	70.3	7.8	70.5	7.9
m-Br	96/1.9	1.5532	90	52.1	5.0	52.2	5.2
MR_3 = $GeEt_3$							
o-Me	119/1.9	1.5330	80	65.4	7.9	65.5	8.1
m-Me	115/1.2	1.5339	82	65.4	8.1	65.5	8.1
p-Bu^t	147/1.9	1.5290	88	68.0	8.7	68.2	8.9
2,3-Me_2	132/1.8	1.5291	80	66.4	8.2	66.5	8.4
2,4,6-Me_3	128/0.8	1.5330	92	67.3	8.5	67.4	8.7
o-OMe	138/2.0	1.5300	84	61.7	7.5	61.9	7.6
m-OMe	140/2.0	1.5390	86	61.9	7.6	61.9	7.6
p-OMe	135/1.2	1.5459	90	62.0	7.3	61.9	7.6
o-Cl	138/2.8	1.5451	88	57.0	6.3	56.9	6.5
m-Cl	128/1.2	1.5430	95	57.0	6.3	56.9	6.5
p-Cl	118/0.9	1.5460	80	56.7	6.3	56.9	6.5
o-Br	138/1.5	1.5570	78	49.3	5.6	49.5	5.65
m-Br	116/0.3	1.5580	85	49.3	5.4	49.5	5.65
p-Br	139/1.5	1.5612	80	49.6	5.6	49.5	5.65
p-F	106/1.6	1.5188	90	60.2	6.8	60.3	6.9
p-I	160/1.8	1.5882	78	43.4	5.0	43.5	5.0
m-CF_3	112/2.6	1.4798	60	54.1	6.1	54.3	6.7

Preparation by the Wurtz-Fittig method. A mixture of *p*-tolylacetylene (0.10 mole), chlorotrimethylsilane (0.12 mole), and toluene (25 ml) was added to a vigorously stirred mixture of sodium (0.24 g-atom) and refluxing toluene (100 ml). After the addition, the mixture was refluxed for 30 min, allowed to cool, and filtered; the filtrate combined with hot-toluene washings of the insoluble material, was fractionated to give trimethyl-(*p*-tolylethynyl)silane, b.p. 116°/16 mm, n_D^{25} 1.5330, in 60 % yield.

Trimethyl(phenylethynyl)silane (53 %) b.p. 214°, n_D^{25} 1.5270, was prepared similarly.

Acknowledgements

This work was supported by the Office of Aerospace Research of the United States Air Force through its European Office. We thank Dr. L. SPIALTER of the Aeronautical Research Laboratory of the Wright Air Development Center, for his interest and encouragement.

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Received February 18th, 1964

Zur Existenz von $(C_6H_5)_2SnLi_2$ und $(C_6H_5)_2Sn(SLi)_2$

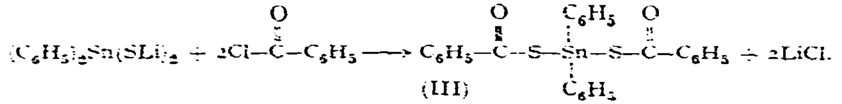
Das aus Triphenylchlorstannan und Lithium erhaltene Lithiumtriphenylstannan reagiert mit elementarem Schwefel in einem Abbaumechanismus unter Bildung von Lithiumtriphenylzinnsulfid[1]. Aus Diphenyldichlorstannan erhielten wir nun mit vier Äquivalenten Lithium in Tetrahydrofuran unter Stickstoff Dilithiumdiphenylstannan (I) nach

$$(C_6H_5)_2SnCl_2 + 4Li \longrightarrow \underset{(I)}{(C_6H_5)_2SnLi_2} + 2LiCl. \tag{1}$$

Die gelbe Lösung des nicht isolierten (I) reagiert mit zwei Äquivalenten Schwefel bei Raumtemperatur sehr rasch unter Bildung einer braunen Lösung von Diphenylzinnbis(lithiumsulfid) (II), wahrscheinlich wieder in einem stufenweisen Abbaumechanismus[1], nach

$$4(C_6H_5)_2SnLi_2 + S_8 \longrightarrow \underset{(II)}{4(C_6H_5)_2Sn(SLi)_2}. \tag{2}$$

Das extrem luft- und feuchtigkeitsempfindliche (II) konnte in Substanz nicht rein isoliert werden (teilweise Bildung von trimerem Diphenylzinnsulfid[2] und Lithiumsulfid). Zum Beweis seiner Struktur wurde es in Lösung mit zwei Äquivalenten Benzoylchlorid umgesetzt. Dabei entsteht Diphenylzinnbis(thiobenzoesäureester) (III) nach



$$(C_6H_5)_2Sn(SLi)_2 + 2Cl{-}\overset{\overset{\large O}{\|}}{C}{-}C_6H_5 \longrightarrow \underset{(III)}{C_6H_5{-}\overset{\overset{\large O}{\|}}{C}{-}S{-}\underset{\underset{\large C_6H_5}{|}}{\overset{\overset{\large C_6H_5}{|}}{Sn}}{-}S{-}\overset{\overset{\large O}{\|}}{C}{-}C_6H_5} + 2LiCl. \tag{3}$$

Das in organischen Lösungsmitteln gut lösliche, nicht besonders hydrolyseempfindliche (III) fällt in Form gelber Kristalle vom Schmp. 142° an.