

ORGANOMETALLIC ACETYLENES OF GROUP IVA ELEMENTS. SYNTHESIS AND SPECTRAL DATA OF TETRAKIS(tert-BUTYLETHYNYL) DERIVATIVES

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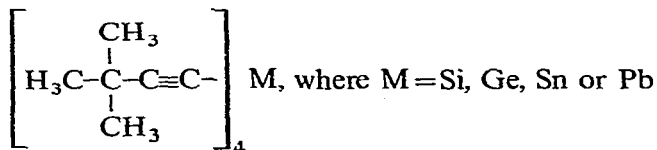
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SUMMARY

The tetrakis(tert-butylethynyl) derivatives of group IVA elements have been synthesized via the reaction of the tert-butylethynyllithium with the tetrachlorides or hexachloro salt in tetrahydrofuran at low temperatures. The expected products were obtained in excellent yields. The tetrakis(tert-butylethynyl) derivatives of silicon, germanium, tin, and lead exhibited a remarkably greater thermal and hydrolytic stability than other corresponding tetraacetylenic derivatives.

A number of publications have appeared during the past few years from our laboratories regarding the synthesis of various types of organometallic acetylenes¹⁻³. In view of our continued efforts and interest in this field coupled with the limited amount of work already reported regarding the synthesis of tetraacetylenic derivatives of silicon, germanium, tin, and in particular, lead^{4,5}, it was thought worthwhile to investigate in detail the syntheses of this class of compounds.

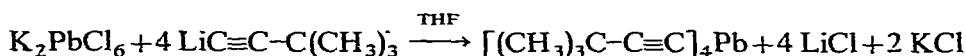
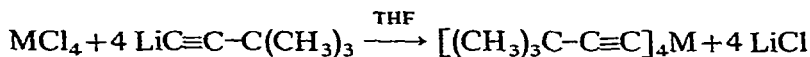
A significant amount of work has already been done on the synthesis and properties of tetraacetylenic derivatives of lead in this laboratory during the past year⁶. A study of the properties of these compounds revealed that most of them are unstable both thermally and hydrolytically. Thus, the approach was directed toward looking for the groups which could have a stabilizing effect on the organometallic tetraacetylenic compound. The literature on the stability of polyacetylenes indicates that these compounds are stabilized by the presence of tertiary butyl groups⁷. Accordingly, we undertook the synthesis of tetrakis(tert-butylethynyl) derivatives of silicon, germanium, tin, and lead. This approach led to a very interesting series of compounds represented by the following structure:



* This paper reports research undertaken at the U.S. Army Natick Laboratories and has been assigned No. 521 in the series of papers approved for publication. The findings in this paper are not to be construed as an official Department of the Army position.

The four new products isolated possess much improved thermal and hydrolytic stability compared with other known tetraacetylenic derivatives of silicon, germanium, tin and lead.

The general reaction for the synthesis of these compounds may be represented as follows:



where M = Si, Ge or Sn

All the reactions were carried out at -78° . The products are obtained in excellent yields. The physical properties and analytical data are summarized in Table 1.

TABLE I

DATA AND ANALYSES OF ORGANOMETALLIC TETRAACETYLIDES^a

Product	Yield (%)	M.p. (°C)	Mol.wt. (in benzene)		Analytical data (%)			
			Found	Calcd.	Found		Calcd.	
					C	H	C	H
$[(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}]_4\text{Si}$	95	181-182	354	353	81.74	10.52	81.75	10.29
$[(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}]_4\text{Ge}$	95	190-191	387	397	72.84	9.22	72.58	9.14
$[(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}]_4\text{Sn}$	96	187-188	438	443	65.10	8.30	65.04	8.19
$[(\text{CH}_3)_3\text{C}-\text{C}\equiv\text{C}]_4\text{Pb}$	85	170-171 (decompn.)	518	531	54.05	6.94	54.20	6.82

^a All the products sublime at: 110-130°/0.05 mm

All these compounds are highly soluble in benzene, tetrahydrofuran and diethyl ether. The silicon and germanium analogs are easily soluble in carbon tetrachloride, whereas the corresponding tin and lead compounds are only partially soluble. The silicon, germanium, and tin analogs could be eluted from a column packed with acidic alumina using petroleum ether. The lead compound in contrast decomposes under the same conditions. The pure compounds could be stored in a refrigerator without any decomposition for indefinite periods of time. Like other tetraacetylenic derivatives these compounds have a tendency to develop color (shades varying anywhere from light yellow to pink) when stored at room temperature in the presence of light.

Thermal stability

The silicon and germanium analogs exhibit remarkable thermal stability. These have sharp melting points, and recrystallize on cooling. Thermal studies indicated no sign of decomposition up to a temperature of 280°.

The corresponding tin compound first melts and then decomposes exothermally. Interesting results were obtained during the thermal studies of tetrakis-(tert-butylethynyl)lead. This compound decomposes exothermally like the tin compound. The tin compound, however, does not decompose even in refluxing decane (b.p. 174°) whereas, the lead derivative has a sharp decomposition temperature (161°)

and yields quantitative amounts of metallic lead. The organic residue is under investigation.

Spectral data

The IR, PMR and Mass Spectral Data are summarized in Table 2.

TABLE 2

SPECTRAL DATA OF THE COMPOUNDS

Compound	IR ^a		PMR ^b	Mass Spectra ^d			
	C≡C stretch	M-C stretch		Parent ion (m/e)	Fragments (m/e)		
	(cm ⁻¹)	(cm ⁻¹)	τ ^c		-Me	-Me ₃ C	-Me ₃ C-C≡C
[Me ₃ C-C≡C] ₄ Si	2164, 2206	775, 942	8.72	352	337	295	271
[Me ₃ C-C≡C] ₄ Ge	2160, 2192	747, 914	8.72	398	383	341	317
[Me ₃ C-C≡C] ₄ Sn	2147, 2178	738, 905	8.72	444	429	387	363
[Me ₃ C-C≡C] ₄ Pb	2142, 2174	734, 902	8.71	532	517		451

^a As KBr pellets. ^b CCl₄ as solvent, TMS as internal standard. ^c For Me₃C-protons; τ=8.79 for Me₃C-C≡CH. ^d For ²⁸Si, ⁷⁴Ge, ¹²⁰Sn and ²⁰⁸Pb.

EXPERIMENTAL

3,3-Dimethyl-1-butyne (Farchan Research Laboratories, USA) was chromatographically pure. Methylolithium (1.7 M) in diethyl ether was obtained from Foote Mineral Co. The tetrachlorides of silicon, germanium, and tin were obtained from commercial sources and purified by distillation. Freshly prepared potassium hexachloroplumbate⁶ was used for the synthesis of corresponding lead derivative. Tetrahydrofuran and diethyl ether were dried over lithium aluminum hydride and distilled under argon prior to use. All reactions were carried out under argon. Molecular weights were determined with a Mechrolab Osmometer Model 301A. The differential thermal data were obtained with a Dupont Model 900. IR spectra were obtained using a Beckman Model IR-12 spectrophotometer, PMR-spectra with a Varian Model A-60, and Mass Spectra using a CEC Model 21-110B.

Preparation of 3,3-dimethyl-1-butyneyllithium

A solution of 13.1 g (0.59 mole) of methylolithium in 350 ml of diethyl ether was placed in a 3-neck flask equipped with a gas inlet, magnetic stirrer and dropping funnel containing 50 g (0.61 mole) of 3,3-dimethyl-1-butyne in 50 ml of diethyl ether. The funnel had an outer cooling jacket to avoid the loss of acetylene (b.p. 36°). The ether solution was added to the stirred methylolithium solution during a period of 45 min at -78°. The contents were then allowed to warm to room temperature. The precipitated lithium salt was filtered and dried under vacuum. A white powder (50 g) was obtained which could be stored under argon without decomposition for a fairly indefinite period of time. The yield was 95%.

Preparation of tetrakis(3,3-dimethyl-1-butyne) derivatives of silicon, germanium and tin

The typical procedure consisted of adding slowly the corresponding tetra-

chloride (0.03 mole) to a stirred suspension of the lithium salt (0.12 mole) (described above) in 250 ml of tetrahydrofuran at -78° . After about an hour the contents were allowed to warm to room temperature. The mixture was stirred at room temperature until the solution became neutral to pH paper. The precipitated lithium chloride was filtered and the solvent was removed under vacuum. The solid obtained was redissolved in benzene to remove any remaining lithium chloride, filtered and dried again. A pink colored solid was obtained in all three cases. The pure white crystalline tetrakis-(tert-butylethynyl) derivatives were then obtained either by sublimation under reduced pressure or recrystallization from $40^{\circ}/60^{\circ}$ b.p. petroleum ether.

For the synthesis of corresponding lead derivative, potassium hexachloroplumbate (0.03 mole) was added in small portions to the stirred suspension of the lithium salt (0.12 mole) in 250 ml of tetrahydrofuran at -78° . The rest of the procedure was the same as described above for the corresponding silicon, germanium and tin compounds. In the latter case, the final product was a white crystalline material which was further purified by sublimation under reduced pressure.

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REFERENCES

- 1 W. E. DAVIDSOHN AND M. C. HENRY, *J. Organometal. Chem.*, 5 (1966) 29.
- 2 W. FINDEISS, W. E. DAVIDSOHN AND M. C. HENRY, *J. Organometal Chem.*, 9 (1967) 435.
- 3 H. F. REIFF, B. R. LALIBERTE, W. E. DAVIDSOHN AND M. C. HENRY, in preparation.
- 4 H. HARTMANN AND M. K. EL A'SSAR, *Naturwissenschaften*, 52 (1965) 304.
- 5 H. HARTMANN AND K. MEYER, *Naturwissenschaften*, 52 (1965) 303.
- 6 B. C. PANT, W. E. DAVIDSOHN AND M. C. HENRY, in preparation.
- 7 R. A. RAPHAEL, *Acetylenic Compounds in Organic Synthesis*, Butterworths, London, 1955, p. 131.
- 8 R. WEST AND C. S. KRAIHANZEL, *Inorg. Chem.*, 1 (1962) 967.

J. Organometal. Chem., 15 (1968) 65-68