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ACETYLENIC DERIVATIVES OF LEAD*

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SUMMARY

Acetylenic derivatives of lead containing one, two or four acetylenic groups around the central lead atom have been synthesized via the reaction of the appropriate lithium acetylide with aryllead halides or potassium hexachloroplumbate in tetrahydrofuran at low temperatures. The expected products were obtained in excellent yields.

INTRODUCTION

In general, tetraalkyl or -aryl compounds of lead have been synthesized by the reaction between lead dichloride and appropriate Grignard or lithium reagents[1-3]. The use of lead tetrachloride as a starting material for synthesizing tetravalent organolead compounds has been avoided primarily because of its instability and also because it is a powerful oxidizing agent. Ammonium, potassium and rubidium hexachloroplumbates have not been systematically studied; however, two different groups of workers have reported the synthesis of tetravinyllead in fairly high yields using the first two reagents[4,5]. The use of rubidium hexachloroplumbate has been reported in synthesizing tetraacetylenic derivatives of lead in poor yields[6,7].

RESULTS AND DISCUSSION

In view of a continuing interest in the synthesis of the acetylides of IVth group elements, we undertook the synthesis of a number of acetylenic lead derivatives containing one, two or four acetylenic groups around the central lead atom. Potassium hexachloroplumbate which can be readily prepared (see *Experimental*) and is stable in the absence of moisture was used for the synthesis of tetraacetylenic lead compounds. Four notable features of the reaction are;

1. Since in most cases the reaction is complete at fairly low temperature, both the likelihood of potential coupling reactions and/or the decomposition of the acetylenic lead compound formed are reduced.

2. The use of pure lithium acetylides rather than their *in situ* generation prevents the formation of undesirable by-products.

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3. The completion of the reaction is easily detected by the disappearance of the yellow color of potassium hexachloroplumbate.

4. The yields of the tetraacetylenic lead derivatives are excellent.

The new acetylenic lead compounds (listed in Table 1) were obtained through the following general reactions:

$$K_2PbCl_6+4\ LiC\equiv CR \rightarrow (RC\equiv C)_4Pb+4\ LiCl+2\ KCl$$
$$(C_6H_5)_2PbCl_2+2\ LiC\equiv CR \rightarrow (C_6H_5)_2Pb(C\equiv CR)_2+2\ LiCl$$
$$(C_6H_5)_3PbCl+LiC\equiv CR \rightarrow (C_6H_5)_3PbC\equiv CR+LiCl$$

All the reactions were carried out in tetrahydrofuran at −78°. The physical properties and analytical data are summarized in Table 1.

Most of the tetraacetylenic and triphenyl monoacetylenic derivatives of lead can be stored without decomposition in the dark in a refrigerator. The compounds have a tendency to turn yellow or red over a very short period of time in the presence of light at room temperature. The diphenyllead diacetylides are very unstable and

TABLE 1

DATA AND ANALYSES OF ORGANOMETALLIC DERIVATIVES

Product	Yield (%)	M.p. (°C)	Analytical data, found (calcd.) (%)		
			Mol. wt.^{a}	C	H
$(CH_3C\equiv C)_4Pb$	71	135–138	—	39.70	3.55
		(decomp.)	(364)	(39.66)	(3.34)
$(C_4H_9C\equiv C)_4Pb$	65	Liquid^b	526	54.15	6.91
			(532)	(54.21)	(6.82)
$(C_8H_{17}C\equiv C)_4Pb$	73	Liquid^b	750	63.91	9.10
			(756)	(63.53)	(9.06)
$(C_6H_5C\equiv C)_4Pb$	65	135	610	63.15	3.32
		(decomp.)	(612)	(62.83)	(3.29)
$[C_6H_5(CH_2)_2C\equiv C]_4Pb$	72	55–56	720	66.40	5.07
		(decomp. 147)	(724)	(66.36)	(5.01)
$(C_6H_{11}CH_2C\equiv C)_4Pb$	70	110	—	62.48	7.51
		(decomp.)	(692)	(62.48)	(7.57)
$[(CH_3)_2CHCH_2C\equiv C]_4Pb$	75	Liquid^b	526	54.21	6.76
			(531)	(54.20)	(6.82)
$[(CH_3)_2CHC\equiv C]_4Pb$	67	95–98	472	50.50	5.91
			(476)	(50.50)	(5.93)
$[(CH_3)_3CC\equiv C]_4Pb$	85	170–171	518	54.05	6.94
			(531)	(54.20)	(6.82)
$(C_6H_5)_2Pb(C\equiv CCH_3)_2$	62	Liquid^b	432	49.12	3.59
			(439)	(49.19)	(3.67)
$(C_6H_5)_2Pb(C\equiv CC_6H_5)_2$	65	85–86	562	59.58	3.33
			(564)	(59.66)	(3.57)
$(C_6H_5)_2Pb(C\equiv CC_8H_{17})_2$	63	Liquid^b	—	60.41	6.96
			(636)	(60.44)	(6.97)
$(C_6H_5)_2Pb[C\equiv CC(CH_3)_3]_2$	65	237	520	55.07	5.35
		(decomp.)	(524)	(55.04)	(5.39)
$(C_6H_5)_3PbC\equiv CC(CH_3)_3$	70	243	530	55.45	4.62
		(decomp.)	(520)	(55.47)	(4.65)

[a] In benzene. [b] Attempted distillation even under reduced pressure resulted in the decomposition of the compound.

in the presence of traces of moisture hydrolyze rapidly to diphenyllead oxide and the parent acetylene and thus totally anhydrous conditions are required for their purification by recrystallization.

All the acetylenic lead compounds turn black and decompose exothermally at their decomposition temperature which is usually close to the melting point. Tetrapropynyllead explodes violently. Only tetrakis(tert-butylethynyl)lead could be sublimed without decomposition. The termal decomposition of these acetylides is an instantaneous process occurring at a very specific temperature.

All the compounds are soluble in benzene, tetrahydrofuran and diethyl ether.

The IR and PMR spectra were found to be as expected. The C≡C stretching frequency (2100–2200 cm^{-1}) for all the lead–acetylenic compounds reported in this paper always occur at a slightly higher frequency than that of the corresponding free acetylene[8].

EXPERIMENTAL

All the acetylenes (Farchan Research Laboratories, USA) were chromatographically pure. Methyllithium (1.7 *M*) in diethyl ether was obtained from Foote Mineral Company. The triphenyllead chloride and diphenyllead dichloride were obtained from the Institute of Organic Chemistry, TNO, Utrecht, The Netherlands. Freshly prepared potassium hexachloroplumbate was used for the synthesis of tetraacetylenic lead derivatives. Potassium hexachloroplumbate was prepared by a modified method of Brauer[9]. Tetrahydrofuran and diethyl ether were dried over lithium aluminum hydride and distilled under argon. Molecular weights were determined with a Mechrolab Osmometer Model 301A. The thermal data, *i.e.*, melting points and decomposition temperatures, were obtained with a duPont Model 900 Differential Thermal Analyzer. Capillary melting points were identical; however, DTA equipment makes it possible to precisely control the heating rate and thus to accurately describe decomposition temperatures. IR spectra were obtained using a Perkin–Elmer 137 spectrophotometer and PMR spectra with a Varian Model A-60.

Preparation of potassium hexachloroplumbate

Concentrated hydrochloric acid (1200 ml) was placed in a 2-liter, two-neck round-bottom flask, equipped with stirrer, powder funnel, and cooled to $-5°$ in an ice/salt bath. Lead dioxide (180 g) was added in small portions. The reaction is exothermic. The temperature was not allowed to rise above $+3°$. The lead dioxide dissolves in the hydrochloric acid with formation of hexachloroplumbic acid and the solution becomes yellow. Towards the end of the lead dioxide addition, the solution turns deep orange and frequently becomes turbid. After the addition was completed, the stirring was stopped. A small amount of a grayish precipitate settled to the bottom of the flask and the supernatant orange-colored liquid was quickly decanted into another 2-liter flask and kept at 0°. Potassium chloride (112 g) dissolved in 400 ml distilled water was added to the stirred hexachloroplumbic acid solution within 5 min. Potassium hexachloroplumbate was formed as a lemon-yellow precipitate. This precipitate was immediately vacuum-filtered through a coarse glass frit, washed on the frit three times with ether (150 ml for each washing) and then air dried, until the product became a free flowing, crystalline yellow powder. If the product is orange colored, it is advisable to dispose of it and repeat the preparation. Yield 250 g (65%). This product contains approximately 80% K_2PbCl_6. It can be purified by dissolving the salt in 20% hydrochloric acid and reprecipitating with hydrogen chloride at 0°. The product is then recovered in a low yield. Since the impurities are inert to our experimental conditions, we found it satisfactory to use the impure potassium hexachloroplumbate directly.

Preparation of lithium acetylide[10]

A solution of methyllithium in diethyl ether was placed in a three-neck flask equipped with a gas inlet, magnetic stirrer and dropping funnel containing a solution of the appropriate acetylene in diethyl ether. The ether solution was added to the stirred methyllithium solution during a period of 30 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 was obtained which could be stored under argon without decomposition for a fairly indefinite period of time. The yield in most cases was about 95%.

Preparation of tetrakis(phenylethynyl)lead

Potassium hexachloroplumbate (4.98 g, 0.01 mole) was added in small portions to the stirred suspension of phenylethynyllithium (4.32 g, 0.04 mole) in 250 ml of tetrahydrofuran at −78° under argon atmosphere. After about an hour the contents were allowed to warm to room temperature. An excess of potassium hexochloroplumbate (1.2 g, about 25%) was then added (after this addition the solution became neutral to aqueous pH paper). The precipitated inorganic salts were filtered and the solvent was removed under vacuum. The solid obtained was redissolved in benzene to remove any remaining inorganic salts, then filtered and dried again. The solid was recrystallized from hot ligroin containing a small amount of benzene.

Preparation of diphenylbis(tert-butylethynyl)lead

Diphenyllead dichloride (8.64 g, 0.02 mole) was added in small portions to the stirred solution of tert-butylethynyllithium (3.52 g, 0.04 mole) in 300 ml of tetrahydrofuran at −78° under an atmosphere of argon. After about 2 h, the contents were allowed to warm to room temperature. The mixture was stirred at room temperature until the solution became neutral to aqueous pH paper (about 1 h). The precipitated lithium chloride was filtered and the solvent was removed under vacuum. The solid obtained was extracted with dry benzene to remove any remaining lithium chloride and finally recrystallized from hot ligroin containing a small amount of benzene.

The liquid products could not be distilled and thus were purified by a conventional treatment with charcoal suspended in anhydrous benzene.

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