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TIN- AND LEAD HYDROCARBONS WITH 1,3-ENYNE RADICALS

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Several acetylenic derivatives of tin and only two acetylenic derivatives of lead have been described in the literature—di(triethyllead)acetylene and di(triphenyllead)acetylene. All these compounds were obtained by the action of the corresponding trialkyl—or triaryl—halides of tin or lead on magnesium, lithium, or sodium acetylides ([1]-[3]). 1,3-Enyne tin and lead hydrocarbons had not been described before our investigations.

Previously we succeeded in obtaining a series of representatives of enyne tin hydrocarbons by the action of trialkyltin halides on magnesium bromovinylacetylene in ether ([4]), but in low yields. It was not possible to obtain enyne lead derivatives by the same method.

Further investigations showed that the tin and lead hydrocarbons of interest to us are obtained in good yields by the action of trialkyltin sodium or trialkyllead sodium on alkenyl bromoacetylenes according to the scheme:

$$R_3Me—Na + Br—C \equiv C—CR' = CH—R'' \rightarrow R_3Me—C \equiv C—CR' = CH—R'' + NaBr,$$

where Me = Sn or Pb, R = CH_3 or C_2H_5, and R′ and R″ = H or CH_3.

Table 1

Constants and analytical data for enyne tin and lead hydrocarbons

Substance	B.p., °C	Pressure, mm	d_4^{20}	n_D^{20}	*MR*, found	*MR*, calc.
$(C_2H_5)_3Sn—C \equiv C—CH = CH_2$	89.5–90.5	10	1.2230	1.5092	62.75	63.20
$(C_2H_5)_3Sn—C \equiv C—CH = CH—CH_3$	104–105	10	1.2183	1.5112	66.66	67.05

Substance	B.p., °C	Pressure, mm	d_4^{20}	n_D^{20}	*MR*, found	*MR*, calc.
$(C_2H_5)_3Sn—C\equiv C—C(CH_3)=CH_2$	97–97.5	10	1.2043	1.5040	66.63	67.05
$(C_2H_5)_3Pb—C\equiv C—CH=CH_2$	114–114.5	6	1.5602	1.5564	66.88	66.80
$(C_2H_5)_3Pb—C\equiv C—C(CH_3)=CH_2$	93–94	3	1.5849	1.5462	71.84	71.45

(continued)

Substance	Found, % C	Found, % H	Found, % Sn(Pb)	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % Sn(Pb)
$(C_2H_5)_3Sn—C\equiv C—CH=CH_2$	—	—	—	—	—	—	—
$(C_2H_5)_3Sn—C\equiv C—CH=CH—CH_3$	48.65	7.46	43.34	$C_{11}H_{20}Sn$	48.76	7.44	43.80
$(C_2H_5)_3Sn—C\equiv C—CH=CH—CH_3$	48.50	7.31	43.60	$C_{11}H_{20}Sn$	48.76	7.44	43.80
$(C_2H_5)_3Sn—C\equiv C—C(CH_3)=CH_2$	48.59	7.86	43.07	$C_{11}H_{20}Sn$	48.76	7.44	43.80
$(C_2H_5)_3Sn—C\equiv C—C(CH_3)=CH_2$	48.50	7.62	43.24	$C_{11}H_{20}Sn$	48.76	7.44	43.80
$(C_2H_5)_3Pb—C\equiv C—CH=CH_2$	34.27	5.42	59.47	$C_{10}H_{18}Pb$	34.77	5.25	59.98
$(C_2H_5)_3Pb—C\equiv C—C(CH_3)=CH_2$	37.37	6.06	57.48	$C_{11}H_{20}Pb$	36.75	5.61	57.64
$(C_2H_5)_3Pb—C\equiv C—C(CH_3)=CH_2$	37.36	5.80	57.22	$C_{11}H_{20}Pb$	36.75	5.61	57.64

Fig. 1. IR transmission spectra (layer thickness 19 μ): **1** —triethylvinylethynyltin, **2** —triethylisopropenylethynyltin, **3** —triethyliso-

Figure 1. IR transmission spectra

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propenylethynyllead, **4** —triethylvinylethynyllead, **5** —triethylisopropenylethynyllead.

This reaction is of interest also because similar acetylenic halogen derivatives usually do not enter into exchange transformations with replacement of the halogen by negatively polarized residues.

The 1,3-enyne tin and lead hydrocarbons obtained by the indicated method are colorless liquids, strongly refracting light, with an unpleasant odor. Their constants are given in Table 1. In pure form, in the absence of air, they remain unchanged for a long time. In air they hydrolyze rapidly. Lead compounds decompose explosively on overheating.

In the infrared spectra, on going from hydrocarbons to analogously constructed compounds of silicon, tin, and lead, a successive lowering of the frequency of the stretching vibrations of the triple bond is observed ($\nu_{C\equiv C}$ for hydrocarbons 2210 cm^{-1}, for silicon hydrocarbons 2150 cm^{-1}, for tin hydrocarbons 2127 cm^{-1}, and for lead hydrocarbons 2110 cm^{-1}), associated not only with the increase in mass of the atoms from carbon to lead, but also with a change in the character of the bond between the acetylenic carbon and the heteroatom (5). The ethylene groupings in the spectra correspond to the usual bands (Fig. 1).

The nuclear magnetic resonance spectra of the tin and lead hydrocarbons differ from the spectra of analogously constructed silicon hydrocarbons by smaller chemical shifts for alkyl radicals bonded to heteroatoms. For silicon hydrocarbons, $\delta_{C_2H_5} = 4.2$ (three peaks); for tin hydrocarbons, 3.8 (three peaks); for lead hydrocarbons, 3.1 (one peak) (Fig. 2).

Attempts to carry out addition reactions at the enyne system of the compounds obtained have so far ended in failure. Under the action of halogens, lithium alkyls, and lithium aluminum hydride, cleavage of the metal–carbon bond occurred. Catalytic hydrogenation apparently did not proceed because of poisoning of the catalyst.

Experimental Part

Triethyltin chloride was prepared by reverse disproportionation from tetraethyltin and $SnCl_4$ (7), and triethyllead bromide by the action of hydrogen bromide on tetraethyllead in petroleum ether (8). Alkenylbromoacetylenes were obtained from the corresponding hydrocarbons and a solution of potassium hypobromite (9, 10).

A dry three-necked flask fitted with a condenser, dropping funnel, and stirrer was charged with liquid ammonia, and triethyltin chloride was added to it dropwise,

Fig. 2. NMR spectra: 1 —triethylvinylethynyltin, 2 —triethylisopropenylethynyltin, 3 —triethylvinylethynyllead, 4 —triethylisopropenylethynyllead

Figure 2: Fig. 2. NMR spectra: 1 —triethylvinylethynyltin, 2 —triethylisopropenylethynyltin, 3 —triethylvinylethynyllead, 4 —triethylisopropenylethynyllead

or triethyllead bromide was introduced. Into the resulting milky-white suspension, over the course of 1 hour, metallic sodium was introduced in small pieces (25% excess). After about half of the calculated amount of sodium had been introduced, in the preparation of tin compounds the solution became transparent and turned lettuce-green, which indicated the formation of hexaethyldistannane. When the remaining amount of metallic sodium was introduced, the solution acquired the dark-green color characteristic of triethyltinsodium, and toward the end, with excess sodium, became blue. In the case of lead compounds, the appearance first of a dirty-green and then of a dark-red color was observed, with a black precipitate forming.

To the resulting solution of triethyltinsodium or triethyllead sodium, with good stirring, the corresponding alkenylbromoacetylene was added dropwise (25% excess). At first the reaction proceeds very vigorously, the color changing to gray in the case of tin and to black in the case of lead. After stirring for 1 hour, ether was added to the mixture. The next day the paste-like mass was heated under a reflux condenser on a water bath until the ammonia had been removed, centrifuged, and the liquid portion was distilled: the ether was distilled off at atmospheric pressure, and the residue was distilled in vacuo. Before distillation it was once again separated from the precipitate. All operations were carried out in a nitrogen atmosphere. The yields were 70–85%.

Fig. 2. NMR spectra: **1** —triethylvinylethynyltin, **2** —triethylisopropenylethynyltin, **3** —triethylvinylethynyllead, **4** —triethylisopropenylethynyllead.

IR spectra were recorded on an IKS-15 spectrophotometer; nuclear magnetic resonance spectra, on an INM-3 instrument.

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