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SYNTHESIS AND REACTIONS OF SOME FUNCTIONALLY SUBSTITUTED ORGANOLEAD COMPOUNDS

HELMUT GORTH* AND MALCOLM C. HENRY
U. S. Army Natick Laboratories, Natick, Massachusetts (U.S.A.)

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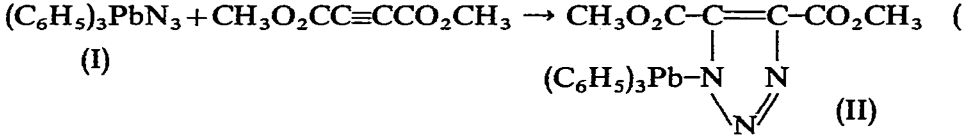
Organolead chemistry is largely concerned with reactions taking place at the lead–carbon bond. Few reactions of organolead compounds are known in which a substituent undergoes reaction without affecting the existing lead–carbon bonds**. Examples of reaction which have been carried out successfully while retaining the lead–carbon structure are Grignard[3], diazonium coupling[4], hydrostannation[5], permanganate oxidation[6,7], and bromination[8] reactions.

Organic azides are known to react readily with carbon–carbon triple bonds to yield triazoles[9] and with activated double bonds to yield triazolines[10,11]. The present work was initiated as a result of a preliminary study of the reaction of triphenyllead azide[12-14] with a number of olefinic and acetylenic compounds. It was found that no reaction took place when triphenyllead azide, (I), was allowed to react in an appropriate solvent with stoichiometric amounts of maleic anhydride, maleic dimethylester, vinyl ethyl ether, morpholinocyclopentene, diphenylacetylene, phenylacetylene, propargyl alcohol or 2-methyl-3-butyn-2-ol. Only with dimethyl acetylenedicarboxylate, a very strong dipolarophile, did the expected reaction take place with the formation of 1-(triphenyllead)-4,5-dicarbomethoxy-1,2,3-triazole, (II)***:



$$(C_6H_5)_3PbN_3 + CH_3O_2CC{\equiv}CCO_2CH_3 \rightarrow CH_3O_2C\text{–}C{=}C\text{–}CO_2CH_3 \quad (1)$$

(I) (II)

From the corresponding bromides a series of organolead alkyl azides were synthesized in which the azido group was displaced from a position immediately adjacent to the lead atom by a carbon chain of successively greater length, $Ph_3Pb\cdot(CH_2)_nN_3$. These azides were then subsequently treated with acetylenic molecules in order to form the corresponding 1,2,3-triazoles.

Willemsens[16] has reported that triphenylleadlithium[17], (III) reacts with polyhalomethanes to yield (triphenyllead)methane derivatives. In an attempt to obtain (haloalkyl)triphenyllead compounds we found that by varying experimental conditions such that triphenylleadlithium reacts with a large excess of dihaloalkanes

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* Present Address: 67 Ludwigshafen/Rhein, Rubinstrasse 15, Germany.

** For reviews in organolead chemistry see ref. 1 and 2.

*** A similar addition of tri-n-butyltin azide to dimethyl acetylenedicarboxylate was reported previously[15].

TABLE 1

REACTION OF TRIPHENYLLEADLITHIUM WITH DIBROMOALKANES

Dibromo-alkane	*Reaction product*	*M.p.* (°C)	*Yield*[a] (%)	*Analysis*	(%) *found* (*calcd.*)		
				Mol. wt.	*C*	*H*	*Pb*
$Br(CH_2)_5Br$	$(C_6H_5)_3Pb(CH_2)_5Br$ (IVa)	61–62	63	588 (583)	46.97 (47.26)	4.28 (4.27)	35.25 (35.27)
$Br(CH_2)_4Br$	$(C_6H_5)_3Pb(CH_2)_4Br$ (Va)	61–63	72	574 (563)	45.99 (46.22)	4.04 (3.86)	36.06 (36.30)
$Br(CH_2)_3Br$	$(C_6H_5)_3Pb(CH_2)_3Br$ (VIa)	62–66	65	560 (563)	45.00 (45.40)	3.77 (3.89)	36.96 (37.20)
$Br(CH_2)_2Br$	$(C_6H_5)_4Pb$[b]	266–228	70				
CH_2Br_2	$(C_6H_5)_3PbCH_2Pb(C_6H_5)_3$ (VII)	98–99.5	73	891 (905)	49.76 (49.93)	3.84 (3.72)	46.50 (46.40)

[a] Yields are based on starting hexaphenyldilead. [b] Tetraphenyllead was identified by TLC, melting point and IR-spectrum.

it was possible to isolate the desired compounds according to the following equation:

$$\underset{\text{(III)}}{(C_6H_5)_3PbLi} + Br(CH_2)_nBr \rightarrow \underset{\text{(IVa)–(VIa)}}{(C_6H_5)Pb(CH_2)_nBr} + LiBr \qquad (2)$$

Dibromomethane and 1,2-dibromoethane were anomalous in their reactions with triphenylleadlithium (Table 1). The reaction of triphenylleadlithium with dibromomethane yielded bis(triphenyllead)methane[16] as the principal product,

$$2\,(C_6H_5)_3PbLi + CH_2Br_2 \rightarrow [(C_6H_5)_3Pb]_2CH_2 + 2\,LiBr\,, \qquad (3)$$

whereas with 1,2-dibromoethane, ethylene[18], tetraphenyllead and lead metal were the main products isolated.

$$(C_6H_5)_3PbLi + BrCH_2CH_2Br \rightarrow (C_6H_5)_3PbBr + C_2H_4 + LiBr \qquad (4a)$$

$$2\,(C_6H_5)_3PbBr + 2\,(C_6H_5)_3PbLi \rightarrow 3\,(C_6H_5)_4Pb + Pb + 2LiBr \qquad (4b)$$

Compounds (IVa), (Va) and (VIa) were converted smoothly to the corresponding azido compound by treatment with excess sodium azide in dimethyl sulfoxide, DMSO, solvent as follows (see Table 2):

TABLE 2

REACTION OF (TRIPHENYLLEAD)ALKYL BROMIDES WITH SODIUM AZIDE

Starting bromide	*Product*	*M.p. (°C)*	*Yield (%)*	*Analysis (%) found (calcd.)*			
				Mol. wt.	*C*	*H*	*N*
(IVa)	$(C_6H_5)_3Pb(CH_2)_5N_3$ (IVb)	oil	[a]	550 (537)	50.16 (50.2)	4.58 (4.55)	7.63 (7.70)
(Va)	$(C_6H_5)_3Pb(CH_2)_4N_3$ (Vb)	42–43.5	68	536 (538)	49.24 (49.0)	4.32 (4.20)	7.83 (7.53)
(VIa)	$(C_6H_5)_3Pb(CH_2)_3N_3$ (VIb)	40.5–42	73	522 (500)	48.26 (48.72)	4.05 (4.19)	8.04 (7.41)

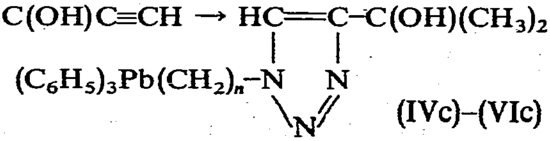
[a] See *Experimental.*

$$(C_6H_5)_3Pb(CH_2)_nBr + NaN_3 \xrightarrow{\text{DMSO}} (C_6H_5)_3Pb(CH_2)_nN_3 + NaBr \qquad (5)$$

(IVa): $n=5$ (IVb): $n=5$
(Va): $n=4$ (Vb): $n=4$
(VIa): $n=3$ (VIb): $n=3$

The infrared spectra of the three azido compounds all show strong azide absorption bands between 2095–2100 cm^{-1} whereas in triphenyllead azide absorption occurs at 2045 cm^{-1}.

(Triphenyllead)alkyl azides, in contrast to triphenyllead azide, undergo 1,3-addition reactions even with weak dipolarophiles such as 2-methyl-3-butyn-2-ol as follows:



$$(C_6H_5)_3Pb(CH_2)_nN_3 + (CH_3)_2C(OH)C{\equiv}CH \rightarrow HC{=}C{-}C(OH)(CH_3)_2 \qquad (6)$$

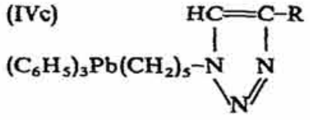
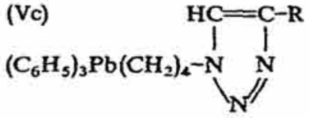
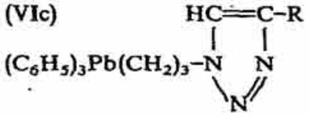
where $n = 3–5$ $(C_6H_5)_3Pb(CH_2)_n{-}N\;\;N$ (IVc)–(VIc)

Since an unsymmetrically substituted acetylene was employed, two isomeric triazole derivatives could be expected with the $(CH_3)_2C(OH)$ moiety in the 4- or 5-position of the triazole ring. There was no indication by thin-layer chromatograms that the compounds were not homogeneous. The long melting ranges, however, might be indicative of the presence of two isomers. The location of the attached moiety remains to be defined and requires further investigation.

Data on the substituted (1-methyl-1-hydroxyethyl)triazoles is shown in Table 3.

TABLE 3

REACTION OF (TRIPHENYLLEAD)ALKYL AZIDES WITH 2-METHYL-3-BUTYN-2-OL

Starting azide	*Product*[a]	*Melting range* (°C)	*Yield* (%)	*Analysis (%) found (calcd.)*			
				Mol. wt.	*C*	*H*	*N*
(IVb)	(IVc) 	62 (softens) to 77–78 (melts)	[b]	634 (645)	53.06 (52.7)	5.24 (5.23)	6.62 (6.48)
(Vb)	(Vc) 	90 (softens) to 120–122 (melts)	65	620 (621)	52.24 (52.15)	5.03 (5.07)	6.76 (6.65)
(VIb)	(VIc) 	95 (softens) to 111–113 (melts)	56	600 (605)	51.44 (51.42)	4.78 (4.92)	6.92 (6.98)

[a] $R = C(OH)(CH_3)_2$. [b] See *Experimental part*.

The infrared spectra of the triazole derivatives indicated the presence of 4 distinct absorptions besides those associated with a normal phenyllead compound[19,20] or 1-methyl-1-hydroxyethyl groups. In the case of (II) the characteristic bands were shifted by the presence of the triphenyllead and carbomethoxy groups attached directly to the triazole nucleus. Tentative assignments in accordance with literature sources[21] are shown in Table 4.

The NMR spectrum of (II) exhibited a multiplet of phenyl protons at 7.5 ppm (TMS = 0) and a singlet for the methyl protons at 3.66 ppm and is therefore consistent with the assumed structure.

TABLE 4

IR ABSORPTIONS (cm^{-1}) ASSIGNED TO VIBRATIONS OF THE TRIAZOLE MOIETY (KBr pellets)

(IVc)	1135[a]	1113[a]	958[a]	853[a]
	1147	1121	966	860
(Vc)	1142	1108	956	858
(VIc)	1123	1103	962	861
(II)	1532	830	802	777

[a] Spectrum recorded in CS_2 solution.

EXPERIMENTAL

Elemental analyses were performed in the analytical laboratories of the U.S. Army Natick Laboratories. Molecular weights were determined with a Mechrolab Osmometer, Model 301A (the solvent was benzene if not otherwise indicated). The infrared spectra were recorded on a Beckman Model IR-12 spectrophotometer and the NMR spectrum with a Varian A60 spectrometer. Melting points are uncorrected. Triphenyllead chloride and hexaphenyldilead were obtained through the auspices of the Lead Industries Association, New York City, N.Y. Reactions involving triphenylleadlithium were carried out under anhydrous conditions in an argon atmosphere. Tetrahydrofuran (THF) was dried by refluxing over lithium aluminum hydride and distilled under argon. The dibromoalkanes were freshly distilled before use.

Triphenyllead azide (I)

Sodium azide, 9.25 g (450 mmole) was added to a solution of 42.7 g (90 mmole) of triphenyllead chloride in 1000 ml of dry acetone and the mixture was stirred for 40 h at room temperature. The contents of the flask were then boiled and filtered hot. The filtrate was evaporated to dryness in vacuum and the remaining residue was extracted with hot benzene in two portions. (I) crystallized from the benzene solution in white needles, m.p. 186–187.5° (yield 30 g, 69%).

1-*Triphenyllead*-4,5-*dicarbomethoxy*-1,2,3-*triazole (II)*

Dimethyl acetylenedicarboxylate, 4.26 g (30 mmole) in 10 ml of benzene was added to a solution of 7.2 g (15 mmole) of (I) in 160 ml boiling benzene. The mixture was refluxed for 2 h during which time (II) started to precipitate as fine white needles. After cooling to room temperature, the crystals were suction filtered and washed with a little benzene. The yield was 7.3 g, m.p., 198–199.5°. The compound is soluble in chloroform and polar solvents. The best method for carrying out a recrystallization of this compound is to dissolve in a 1 : 1 benzene/ethanol mixture and then evaporate the solvents slowly. Found: C, 46.60; H, 3.51; N, 6.78; mol. wt. in chloroform, 639. $C_{24}H_{21}N_3O_4Pb$ calcd: C, 46.29; H, 3.39; N, 6.75%; mol. wt., 622.

Triphenylleadlithium[17] *(III)*

Hexaphenyldilead, 21.95 g, (25 mmole) was dissolved in 90 ml of THF. Lithium wire coated with paraffin oil (1.2 g, 200 mmole) was hammered flat (to obtain a larger surface), finely cut, washed with THF and added to the stirred organolead solution. The large excess of lithium was used to make sure that all hexaphenyldilead was cleaved, since unreacted hexaphenyldilead is difficult to remove from the reaction products of (III) with the dibromoalkanes. After an induction period the temperature of the darkening reaction mixture rose, reached 60° within 20 min and then dropped slowly. After stirring for 3.5 hours the black suspension was filtered through a tube filled with glass wool into a dropping funnel.

Reactions of (III) with dibromoalkanes

The above mentioned freshly prepared solution of 50 mmoles (III) was slowly dropped into a stirred solution of 250 mmoles of the appropriate dibromoalkane in 20 ml of THF at room temperature. The reaction was slightly exothermic. After the addition was completed (*ca.* 40 min), stirring was continued for 1.5 hours and then the dark mixture was poured into a saturated aqueous ammonium chloride solution. Chloroform was added and the organic layer was separated. The aqueous layer was extracted twice with chloroform and the combined organic extracts were washed with water and dried over magnesium sulfate. The solvent was removed in vacuum leaving behind a semi-crystalline yellow residue. The yellow impurity could be removed by column-chromatography using about 75 g of neutral alumina per 10 g. (VII) obtained in this manner was evaporated in vacuum to complete dryness and the residues were dissolved in boiling hexane, leaving behind a small amount of tetraphenyllead. The compounds crystallized readily from the cooled, filtered hexane.

(Triphenyllead)alkyl azides

Sodium azide, (4.9 g, 75 mmole) was dissolved in 60 ml of dimethyl sulfoxide at 80–90°. To this solution 15 mmole of the appropriate (triphenyllead)alkyl bromide was added and the mixture was stirred for 2.5 h at 90°. After cooling to room temperature ether and water were added until two clear layers were formed. The layers were separated, the aqueous part was extracted twice with ether and the combined organic extracts were washed three times with water. The ether solution was first dried over magnesium sulfate and then the ether solvent was evaporated. The remaining oil was dissolved in boiling hexane and the solution was cooled to $-20°$. (Vb) and (VIb) were thus obtained in crystalline form and could be recrystallized. (IVb) separated as an oil. Part of this liquid was chromatographed on neutral alumina (hexane $+20\%$ benzene) and after removal of the solvent by evaporation, an oil was obtained. Since this purification involved considerable loss of substance, only a small part was purified for analytical purpose and the crude oil was used for further reaction. The yield of (IVb) was about the same as of (Vb) and (VIb) since the weight of the crude products was approximately the same.

[(Triphenyllead)alkyl]triazoles

Compounds (IVb), (Vb) or (VIb) (5 mmoles), were refluxed in 10 g of 2-methyl-3-butyn-2-ol for 6 h. After removing the excess butynol under vacuum, the remaining oil was taken up in hot chloroform. The filtered chloroform solution was boiled and treated with hot hexane until it became cloudy. (Vc) and (VIc) crystallized readily; (IVc) separated as an oil. Portions of (IVc) were purified the same way as (IVb). (Chloroform followed by chloroform $+10\%$ methanol were the elution solvents.) The oil so obtained started to crystallize after standing for 2 weeks. The yield of (IVb) was approximately the same as that of the two other compounds, since the weight of the crude products was about the same.

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SUMMARY

A series of (triphenyllead)alkyl bromides has been converted to the corresponding azido compounds. The azido compounds were in turn combined with acetylenic derivatives to yield a series of organolead substituted triazoles. Anomalous behavior of the lower molecular weight derivatives has been noted and discussed.

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