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PREPARATION OF BUTADIENYL- AND BUTENYL-PLUMBANES AND -STANNANES, BY HYDROPLUMBYLATION AND HYDROSTANNYLATION OF VINYLACETYLENE AND 1-BUTYNE INCLUDING *IN SITU* TECHNIQUES*

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SUMMARY

Methods of preparation of butadienylplumbanes or -stannanes by reactions of vinylacetylene (1-buten-3-yne) with alkyllead and alkyltin hydrides are described. A procedure was developed for *in situ* butadienylation by addition of lithium aluminum hydride to a mixture of alkylmetal halide and 1-buten-3-yne. In a similar fashion butenylation by addition to 1-butyne was developed.

Tripropyl(1-buten-1-yl)tin, triphenyl(1-buten-1-yl)tin, tripropyl(1,2-butadien-1-yl)tin, triphenyl(1,2-butadien-1-yl)tin, dibutyl(di-1-buten-1-yl)tin, triethyl(1-buten-1-yl)lead, and triethyl(1,3-butadien-1-yl)lead have been prepared. In all cases, the organometal hydride adds to 1-butyne as one would predict if a free radical mechanism were operative, *i.e.*, via anti-Markovnikov addition. The organotin hydrides add in a 1,4-manner to vinylacetylene forming allenic derivatives while the organolead hydride adds to vinylacetylene to give the 3,4-addition product. The latter may be formed by 1,4-addition followed by rearrangement.

INTRODUCTION

An *in situ* hydroplumbation of alkynes such as acrylonitrile involving an initial exchange reaction between trialkyltin hydrides and trialkyllead salts has been described by Creemers and coworkers[1]. These authors have reported that the use of $LiAlH_4$ instead of trialkyltin hydride has afforded organolead adducts in very poor yields. We have investigated this general reaction for the preparation of a hydride of a Group IV metal by reaction of $LiAlH_4$ and the trialkylmetal salt and the *in situ* addition to an olefin. Since our objective was to prepare butadiene derivatives of lead and tin, the olefin investigated was vinylacetylene.

Addition of stannyl hydrides[2,3,4] and alkali metal stannanes[5,6,7] to enynes has been reported as a potential method for the preparation of butadienylstannanes. This paper deals with several preparative methods which provide facile syntheses of 1-butadienyl- and 1-butenyl-stannanes and -plumbanes. Trialkyltin salts and 1-butyne

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* Taken from the M. S. Thesis of S.J.H.

were used to simplify initial studies. Most lead hydrides are relatively unstable and not isolable at room temperatures, which makes the *in situ* addition particularly useful for the formation of plumbanes.

RESULTS AND DISCUSSION

Tripropyl(1-buten-1-yl)tin, triphenyl(1-buten-1-yl)tin, tripropyl(1,2-butadien-1-yl)tin, triphenyl(1,2-butadien-1-yl)tin, dibutylbis(1-buten-1-yl)tin, triethyl(1-buten-1-yl)lead and triethyl(1,3-butadien-1-yl)lead (see Table 1) have been prepared by permitting the corresponding organometal hydride to react with either 1-butyne (Eq. 1) or vinylacetylene (Eq. 2 and 3).

Butyne: 1,2-*addition*

$$R_3MH + HC{\equiv}C{-}C_2H_5 \rightarrow R_3M{-}CH{=}CH{-}C_2H_5 \tag{1a}$$

$R = C_3H_7,\ M = Sn$

$R = C_6H_5,\ M = Sn$

$R = C_2H_5,\ M = Pb$

$$R'_2MH_2 + HC{\equiv}C{-}C_2H_5 \rightarrow R'_2M(CH{=}CHC_2H_5)_2 \tag{1b}$$

$R' = C_4H_9,\ M = Sn$

Vinylacetylene: 1,4-*addition*

$$R_3MH + HC{\equiv}C{-}CH{=}CH_2 \rightarrow R_3M{-}CH{=}C{=}CHCH_3 \tag{2}$$

$R = C_3H_7,\ M = Sn$

$R = C_6H_5,\ M = Sn$

Vinylacetylene: 3,4-*addition*

$$R_3MH + HC{\equiv}C{-}CH{=}CH_2 \rightarrow R_3M{-}CH{=}CH{-}CH{=}CH_2 \tag{3}$$

$R = C_2H_5,\ M = Pb$

Butadienyl compounds of Group IV metals are difficult to prepare and have only recently been reported[2,8,9]. A step-wise investigation of reaction conditions was made to study the possibility of an *in situ* metal hydride addition to alkynes and also to investigate its specific application for the preparation of butadienyl metallanes. These reaction conditions are outlined below:

A. A sealed tube reaction of the corresponding hydride and alkyne, neat, at 100° with either 2,2′-azobis(2-methylpropionitrile) or benzoyl peroxide as an initiating agent. (The conditions of Satgé *et al.*[10] for the addition of alkylmetal hydrides to olefins.)

B. Reaction at atmospheric pressure (under nitrogen) of the corresponding hydride and alkyne at 66° (boiling THF) using either of the above initiators.

C. Reaction at atmospheric pressure (under nitrogen) of the organometallic salt, alkyne, and lithium aluminum hydride using inverse addition; *i.e.*, $LiAlH_4$ dissolved in a solvent was added dropwise to a solution of the organometallic salt and alkyne.

TABLE 1

UNSATURATED PLUMBANE PRODUCTS

Compound	*Yield (%)*[a] *method of preparation*	*Appearance and b.p. (°C/mmHg) or m.p. (°C)*	*Analysis Found (calcd.) (%)*		*Major IR peaks (cm^{-1})*				*Behavior on treatment with alcoholic AgNO$_3$*
			C	*H*					
$Pr_3SnCH{=}CHCH_2CH_3$	85/A 93/B 38/C	Colorless Liquid 70–73/0.5–1	51.70 (51.50)	9.21 (9.03)	1820		1380	1640	Brown → black
$Pr_3SnCH{=}C{=}CHCH_3$	70/A 13/C	Pale yellow liquid 80–90/1–2	52.01 (51.88)	8.80 (8.64)	1820	1960	1380	1560	Yellow $\xrightarrow{\text{slow}}$ black
$Ph_3SnCH{=}CHCH_2CH_3$	100/B	White solid room temp.	65.01 (65.20)	5.33 (5.23)	1820		1380	1640	Brown $\xrightarrow{\text{yellow}}$ green
$Ph_3SnCH{=}C{=}CHCH_3$	100/B	Yellow solid room temp.	63.32 (65.56)	5.03 (4.97)	1820		1380	1590	Yellow → olive
$Bu_2Sn(CH{=}CHCH_2CH_3)_2$	27/C	Colorless liquid 100–105/1	55.06 (55.68)	9.04 (9.83)	1820		1380	1640	Orange → brown
$Et_3PbCH{=}CHCH_2CH_3$	10/C	Colorless liquid 56–58/0.5–1	35.35 (35.36)	6.20 (6.34)	1850	1160	1380	1640	Brown → black
$Et_3PbCH{=}CH{-}CH{=}CH_2$	31/C	Pale Yellow Liquid 45–50/0.5			1850	1160	1380	1590	Brown → black

[a] Yields for method A based upon starting hydride. Yields for method B based upon starting hydride. Yields for method C based upon starting organometal chloride.

Triethyllead hydride has previously been prepared in only 20% yield and decomposes at $-20°$[11]. Therefore, the yields in the *in situ* procedure C (see Table 1) involving this intermediate are considered quite good.

The free radical initiator was omitted in procedure C. Such an initiator would be unnecessary for triethyllead hydride which is known to decompose homolytically at less than 0°[10]. Mal'tseva *et al.* have reported[2] that the addition of 15 mole % hydroquinone as an inhibitor or less than 25 mole % of 2,2'-azobis(2-methylpropionitrile) as an initiator failed to noticeably change the course of hydrostannylation of alkenyne hydrocarbons. This apparent independence of initiator has also been described by Leusink and Marsman[12]. The rate of hydrostannylation strongly depends upon the polarity of the solvent, implying that something other than a free radical mechanism may be operative[13].

Satgé *et al.*[10] have shown that addition of Group IV metal hydrides to conjugated dienes seems to proceed via a 1,4-addition rather than 1,2-addition. This has been illustrated by the addition of trimethylgermane to butadiene to yield trimethyl-(2-buten-1-yl) germane[11]. Trimethyltin hydride has been treated with 1,3-butadiene to yield a mixture of 93% 1,4-addition product along with 7% of 1,2-addition product[15]. Mal'tseva *et al.*[2] reported a yield of 60–70% product by 3,4-addition of triethyltin hydride to vinylacetylene (Eq. (3) $R = C_2H_5$ $M = Sn$).

In contrast, we have not isolated any butadienyltin products resulting from 3,4-addition of a tin hydride to vinylacetylene nor have we isolated any products resulting from 1,2-addition to the terminal vinyl group, or acetylene substitution products (Eq. 4b) as reported by Mal'tseva *et al.*[1,2]. Under our reaction conditions,

$$R_3MH + CH\equiv C-CH=CH_2 \rightarrow \begin{cases} R_3M-CH_2CH_2-C\equiv CH & \text{(4a)} \\ R_3M-C\equiv C-CH=CH_2. & \text{(4b)} \end{cases}$$

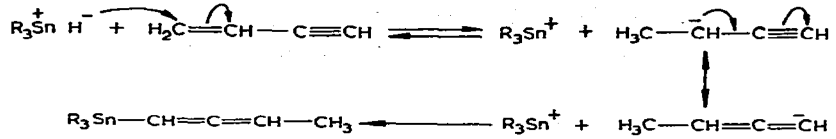
1,4-addition occurs to the extent of ca. 70% as compared to 9% as reported by Mal'tseva[2]. Kakhniashvili and Ioramashivili[16] have shown in the hydrosilylation and hydrogermylation of 5-methoxy-5-methyl-1-hexen-3-yne with chloroplatinic acid catalysis that allene formation is favored at lower temperatures. Possibly their reported 1,2-addition product arises from rearrangement of the allene to the more thermally stable conjugated butadiene.

Boranes have been reported to react more rapidly with isolated ethylenes than with isolated acetylenes. However, when both groups are in the same molecule, boranes react exclusively with the acetylene group[17]. With one exception[2] in the reported additions of Group IV hydrides to enynes, the organometal hydride attacks the acetylenic group in preference to the ethylenic group[18a]. Our work is consistent with the above observation.

An extended Hückel calculation, which is to be published separately, indicates that the 1-substituted 4-allenyl free radical is more stable than the 1-substituted 2-(1,3-butadienyl) free radical. The stability and rearrangements of stannyl-substituted free radicals is well documented[14] and offers a ready explanation of the observed 1,4-addition, *i.e.*, reaction via rearrangement to the most stable radical (Eq. 5).

$$\begin{tikzcd} R_3Sn\cdot + HC\equiv C-CH=CH_2 \arrow[r, shift left] & R_3SnCH=\dot{C}-CH=CH_2 \arrow[l, shift left] \arrow[d, shift right] \\ R_3Sn\cdot + R_3SnCH=C=CHCH_3 & R_3SnCH=C=CH-\dot{C}H_2 \arrow[l, "R_3SnH"'] \arrow[u, shift right] \end{tikzcd} \qquad (5)$$

An ionic mechanism for hydrostannylation has also been shown to be operative in the case of substituted and highly activated alkynes[13]. This type of mechanism could be important in the case of the highly polarizable vinylacetylene as illustrated in Eq. 6.


(6)

The conjugated product observed in the lead series but not in the tin series may result from rearrangement of an intermediate allene (Eq. 7) and may be expected in light of bond energy considerations.

$$R_3Pb{-}CH{=}C{=}CH{-}CH_3 \rightarrow R_3Pb{-}CH{=}CH{-}CH{=}CH_2 \qquad (7)$$

The dissociation energy of a Pb–C bond is at least 15 kcal/mole less than that of a Sn–C bond, leading to the conclusion that free radical reactions involving lead are much more reversible than those reactions involving tin[18b].

Evidence for the direction of addition and the position of substitution has been achieved by study of the infrared spectra of several of the tin compounds reported herein. The infrared spectrum of triphenyl(1,2-butadien-1-yl)tin showed absorption at 1471 and 1431 cm^{-1} identical with that shown by the triphenyltin hydride starting material. Methyl absorption (1380 cm^{-1}) and non-methylene absorption (1450 cm^{-1}) were observed in the spectrum of the product. Triphenyl(1,2-butadien-1-yl)tin also shows allene absorption at 1960 cm^{-1}. Aufdermarsh[19] has reported this adsorption to be detectable for allene solutions with concentrations as low as 0.3 %. This evidence is further confirmation of the allenic structure of the tin products and substantiates attack of the trialkyltin radical at the acetylene group rather than the vinyl group. The terminal attachment of the tin in the tripropyl and triphenyl derivatives is also supported by strong infrared absorption in both spectra attributed to C=C stretch (1610 cm^{-1}, shifted to a longer wave length by metal substitution) and an absence of terminal vinyl absorption (980 and 925 cm^{-1}) expected for compounds with tin attached at the 2-carbon.

Addition of triethyllead hydride to 1-butyne proceeded in a normal manner to give terminal substitution. The infrared spectrum shows C=C stretching at 1610 cm^{-1} and the absence of absorption at 980 and 925 cm^{-1} for a terminal vinyl. The reaction of triethyllead hydride and vinylacetylene gave the 3,4-addition product, triethyl-(1,3-butadien-1-yl)lead identical with an authentic sample[8]. Whether this conjugated system arises from direct 3,4-addition or from 1,4-addition with subsequent rearrangement is not known at this time. If any triethyl(1,2-butadien-1-yl)lead was present in the reaction mixture, its concentration was less than 0.3 %[19], as indicated by the absence of allene absorption at 1956 cm^{-1} in the infrared spectrum.

EXPERIMENTAL

Starting Materials

trans-1,4-Dichloro-2-butene was obtained from Eastman Kodak Company and was used as received. 1-Butyne was obtained from Matheson Company, Inc., and was condensed in a Dry Ice–acetone bath before use. Vinylacetylene was prepared from *trans*-1,4-dichloro-2-butene[20]. Tetraethyllead was obtained from the Ethyl Corporation and used as received. Tri-n-propyltin chloride, triphenyltin hydride and dibutyltin dichloride were obtained from Alfa Inorganics, Inc., and were used as received. Triethyllead chloride was synthesized by the established procedure of Gilman and Robinson[21]. Tetrahydrofuran was purified by distillation from lithium aluminum hydride.

Gas Chromatography

The analytical samples of tripropyl(1-buten-1-yl)tin, tripropyl(1,2-buten-1-yl)-tin, dibutyl(di-1-buten-1-yl)tin and triethyl(1-buten-1-yl)lead were obtained by gas–liquid chromatography. The chromatograph used was an Aerograph Manual Temperature Programmer gas chromatograph, model A-90-P. The column used was a 3′ × 1/4″ aluminum column packed with 20% diisodecyl phthalate on 45/60 mesh chromosorb P. The injector temperature was 130°, the oven temperature was 110°, and the detector temperature was 145°. The flow rate was 60 ml per min.

Procedure A

The appropriate alkylmetal hydride and alkyne were mixed in a 1/2 molar ratio in a glass vial. 2,2′-Azobis(2-methylpropiononitrile) (0.4 mole %) or benzoyl peroxide was added as a free radical initiator. The vial was flushed with nitrogen, sealed, and heated in a boiling water bath for 4 h, at which time the vial was removed, cooled and opened. The contents of the vial were fractionally distilled under vacuum.

Procedure B

A three-necked flask was equipped with a Dry Ice–acetone cooled condenser, a pressure equalizing addition funnel, a magnetic stirrer, and the reaction was conducted under a nitrogen atmosphere. A solution of the appropriate alkyne and alkylmetal hydride (5/1 molar ratio) in dry tetrahydrofuran (500 ml of THF per 0.5 mole of alkyne) was run into the flask. Free radical initiator (0.4 mole %) was added and the mixture was heated for 3 h on a water bath maintained at 70°. The reaction mixture was subsequently cooled, stripped of solvents and the high boiling residue fractionally distilled under vacuum.

Procedure C

The apparatus used for the procedure was the same as in Procedure B. The flask was charged with solvent* (50 ml per 0.2 mole of alkyne), the appropriate alkylmetal chloride and alkyne (1/2 molar ratio of chloride to alkyne). Rapid stirring was initiated. The optimum reaction temperature** was maintained by use of a water bath. Lithium aluminum hydride (1/1 molar ratio of $LiAlH_4$ to alkylmetal chloride) was suspended in solvent (100 ml per 0.1 mole $LiAlH_4$) and was added dropwise to the rapidly stirred mixture in the reaction flask. After addition of the lithium aluminum hydride suspension was complete, the mixture was stirred for an additional 2 h. Sub-

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* The solvent used for trialkyllead chloride was diethyl ether; for trialkyltin chloride, tetrahydrofuran was used.

** The temperature used for production of lead compounds was 0°; for tin compounds, the reflux temperature of tetrahydrofuran was chosen.

sequently, the reaction mixture was treated at 0° with 1 g of hydroquinone. Sodium potassium tartrate (20%) solution, equi-vol with ether, was added very slowly to quench the reaction. The resulting layers were separated and the aqueous layer was extracted with sufficient ether to remove all organometallics from the aqueous layer as indicated by alcoholic silver nitrate test. The organic extracts were combined and dried over anhydrous sodium sulfate. The solvent was removed and the crude product was fractionally distilled under vacuum.

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