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ORGANOMETALLIC ACETYLENE CHEMISTRY
II. DISUBSTITUTED ACETYLENES OF THE TYPE $R_3MC{\equiv}CM'R_3$*

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Disubstituted organometallic acetylenes of the fourth main group are numerous, but only two have been reported which have two different Group IV metal atoms in the same molecule[1,2]. Several synthetic routes can be utilized for the preparation of such "mixed" organometallic acetylenes:

$$R_3MC{\equiv}CH \xrightarrow{M'' \text{ or } RMgBr} R_3MC{\equiv}CM''(MgBr) \xrightarrow{R_3M'X} R_3MC{\equiv}CM'R_3 \quad \text{(refs. 1, 3, 4)} \quad (1)$$

$M'' = $ Alkali metal; $X = $ Halogen

$$R_3SnOSnR_3 + 2\,HC{\equiv}CMR_3 \rightarrow 2\,R_3SnC{\equiv}CMR_3 + H_2O \quad \text{(ref. 2)} \quad (2)$$

$$R_3MNR_2 + HC{\equiv}CM'R_3 \rightarrow R_3MC{\equiv}CM'R_3 + HNR_2 \quad \text{(refs. 5, 6)} \quad (3)$$

$$R_3MC{\equiv}CMR_3 + R'Li \xrightarrow{XM'R_3} R_3MC{\equiv}CM'R_3 + R'MR_3 + LiX \quad \text{(ref. 7)} \quad (4)$$

$M, M' = $ different Group IV metals

We have now found a convenient route to these "mixed" organometallic acetylenes by a two-step procedure, and have prepared a series of such compounds with different Group IV organometallic moieties. The preparation and reactions of the starting aminostannanes and aminoplumbanes have been reported[5,8,9]. They react smoothly and quantitatively with acetylenic compounds that contain a proton adjacent to the triple bond.

RESULTS AND DISCUSSION

During our investigation of the scope and limitations of the synthesis of organometallic acetylenes by use of sodium acetylide, a facile method was found to prepare "mixed" disubstituted acetylenes of the type $R_3MC{\equiv}CM'R_3$ where M and M' are different fourth group elements.

The simplest procedure consists in treating a fourth group organometalamino compound with sodium acetylide. The resulting mixture is allowed to react directly with a trialkyl- or triarylmetal halide that contains a different fourth group element.

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The overall conversion is represented by eqn. (5).

$$R_3MNR'_2+NaC{\equiv}CH+R_3M'Cl \rightarrow R_3MC{\equiv}CM'R_3+R'_2NH+NaCl \tag{5}$$

When the reaction is conducted in this manner two different courses can be formulated. The first involves the initial reaction of the organometalamino compound with sodium acetylide to give the corresponding organometalethynylsodium. This intermediate then reacts with the organometallic halide that contains the other fourth group metal to yield the "mixed" acetylene.

$$R_3MNR_2+NaC{\equiv}CH \rightarrow R_3MC{\equiv}CNa+R_2NH_2 \tag{6}$$

$$R_3MC{\equiv}CNa+R_3M'X \rightarrow R_3MC{\equiv}CM'R_3+NaX \tag{7}$$

Alternatively the reaction could proceed by a second course in which the organometalalkyne is the primary product (eqn. 8), which then reacts with the organometalamino compound according to eqn. (3).

$$R_3MCl+NaC{\equiv}CH \rightarrow R_3MC{\equiv}CH+NaCl \tag{8}$$

The reaction of triphenyl(diethylamino)stannane or triphenyl(diethylamino)-plumbane with sodium acetylide gave the sodium derivatives of the corresponding (triphenylmetal)ethynyl compounds, which could be isolated in an inert atmosphere. (Triphenylsilyl)(triphenylstannyl)acetylene and (triphenylsilyl)(triphenylplumbyl)-acetylene were obtained in good yield by a treatment of their respective sodium salts with triphenylchlorosilane.

These observations indicate that the formation of the "mixed" acetylenes probably proceeds by the first course, which involves the initial reaction of the organometalamino compound with sodium acetylide, at least in those instances where the intermediate sodium salt has been isolated. The sequence of reactions is not clear in the case of triphenyl(diethylamino)germane, since the intermediate sodium derivative could not be isolated. Treatment of the crude reaction mixture with triphenylchlorosilane gave only a poor yield of (triphenylsilyl)(triphenylgermyl)acetylene.

(Triphenylsilyl)(triphenylgermyl)acetylene was also prepared in moderate yield by an alternate method (eqn. 4) which consists of cleaving bis(triphenylsilyl)-acetylene with butyllithium. The resulting (triphenylsilyl)ethynyllithium was treated with triphenylbromogermane (eqn. 4a, 4b).

$$(C_6H_5)_3SiC{\equiv}CSi(C_6H_5)_3+n\text{-}BuLi \rightarrow (C_6H_5)_3SiC{\equiv}CLi+n\text{-}BuSi(C_6H_5)_3 \tag{4a}$$

$$(C_6H_5)_3SiC{\equiv}CLi+BrGe(C_6H_5)_3 \rightarrow (C_6H_5)_3SiC{\equiv}CGe(C_6H_5)_3+LiBr \tag{4b}$$

We propose to further study these interesting alkali metal derivatives of the fourth group organometallic acetylenes, and present the results in a later publication.

Data for the symmetrical and "mixed" organometallic acetylenes are listed in Table 1.

An estimate of the thermal stabilities of the comparable aryl compounds of Table 1 was obtained by visual determination of the decomposition point in a capillary tube. Despite the occasional appearance of an initial turbidity the onset of decomposition as shown by blackening was fairly sharp. Bis(triphenylsilyl)acetylene and bis-(triphenylgermyl)acetylene did not decompose below 350°. The tin-containing compounds of the series [(III), (VI), (VIII)] decomposed in the range 290–310°,

TABLE 1

DATA AND ANALYSIS OF ORGANOMETALLIC "MIXED" ACETYLIDES

Compounds	*Yield* (%)	*M.p./b.p. (mm)* (°C)	*Mol. wt.* *Calcd.*	*Found*	*C (%)* *Calcd.*	*Found*	*H (%)* *Calcd.*	*Found*
(I) $(C_6H_5)_3SiC{\equiv}CSi(C_6H_5)_3$[a]		156						
(II) $(C_6H_5)_3SiC{\equiv}CGe(C_6H_5)_3$	42	151	587	571	77.72	77.75	5.15	5.31
(III) $(C_6H_5)_3SiC{\equiv}CSn(C_6H_5)_3$	64	124–126	633	609	72.09	72.00	4.78	4.87
(IV) $(C_6H_5)_3SiC{\equiv}CPb(C_6H_5)_3$	59	128–129	722	738	63.23	62.65	4.19	4.26
(V) $(C_6H_5)_3GeC{\equiv}CGe(C_6H_5)_3$[b]		148–149						
(VI) $(C_6H_5)_3GeC{\equiv}CSn(C_6H_5)_3$	87	149	678	662	67.32	67.12	4.46	4.49
(VII) $(C_6H_5)_3GeC{\equiv}CPb(C_6H_5)_3$	58	134–135	766	811	59.59	58.90	3.94	3.85
(VIII) $(C_6H_5)_3SnC{\equiv}CSn(C_6H_5)_3$[a]		152						
(IX) $(C_6H_5)_3SnC{\equiv}CPb(C_6H_5)_3$		143–145	812	815	56.24	55.67	3.73	3.66
(X) $(C_6H_5)_3PbC{\equiv}CPb(C_6H_5)_3$[a]		139						
(XI) $(CH_3)_3SiC{\equiv}CGe(CH_3)_3$[c]		25/150–151(750)						
(XII) $(CH_3)_3SiC{\equiv}CSn(CH_3)_3$	68	24–25/25(1)	261	262	36.82	37.00	7.14	6.95
(XIII) $(CH_3)_3GeC{\equiv}CSn(CH_3)_3$	40	41–44/47(1)	305	320	31.45	31.11	5.94	5.83

[a] Ref. 10. [b] Ref. 11. [c] Ref. 1.

and the lead-containing members [(IV), (VII), (IX), (X)] at 210–225°. Bis(triphenylplumbyl)acetylene (X) undergoes decomposition at its melting point.

The attempted preparation of bis(trimethylplumbyl)acetylene gave a grey, crystalline material which was successfully sublimed at 100° under 1 mm pressure. When an attempt was made to resublime 3 g of the product under the same conditions, it detonated with sufficient violence to destroy the surrounding equipment.

Table 2 comprises data obtained from the infrared and NMR spectra of several of the "mixed" organometallic acetylene. With the exception of the three tabulated compounds the acetylenic absorption was too weak to be observed in the mid-infrared region (2–16 μ). This was probably a result of the almost symmetrical substitution of the acetylene bond.

TABLE 2

IR AND NMR DATA

Compound	*C≡C Stretch* (cm^{-1})	*NMR (TMS Standard, 60 Mcps)*	
$(C_6H_5)_3SiC{\equiv}CPb(C_6H_5)_3$[a]	2074		
$(CH_3)_3SiC{\equiv}CSn(CH_3)_3$	2079	$\delta[CH_3(Si)]$ 7 cps	$\delta[CH_3(Sn)]$ 15 cps
$(CH_3)_3GeC{\equiv}CSn(CH_3)_3$	2075	$\delta[CH_3(Ge)]$ 19 cps	$\delta[CH_3(Sn)]$ 15 cps

[a] The C≡C stretching vibration of this compound was obtained as a very weak band in a concentrated chloroform solution.

EXPERIMENTAL

The molecular weights in benzene were obtained on a Mechrolab vapor-pressure osmometer Model 301A. Infrared spectra were recorded on a Beckman IR-12. The NMR data were obtained with a Varian A-60 spectrometer. Melting points are not corrected and were observed on a Thomas Hoover melting point apparatus.

All reactions were carried out under argon and under absolutely anhydrous conditions. Sodium acetylide, trimethylchlorosilane and triphenylchlorosilane were commercially available products. The other triphenylmetal halides were prepared from the tetraphenylmetal compounds according to published procedures. Trimethylchlorogermane was prepared from tetramethylgermane and gallium trichloride[12].

$$(CH_3)_4Ge + GaCl_3 \rightarrow (CH_3)_3GeCl + CH_3GaCl_2$$

The transmetalation reaction was used for the preparation of the aminometal compounds[8]. Tetrahydrofuran and diethyl ether were dried with lithium aluminum hydride and distilled under argon. Diethylamine was distilled over potassium hydroxide shortly before each use.

Preparation of trimethylethynylsilane

Trimethylchlorosilane was dissolved in anhydrous pyridine, added to a suspension of an equimolar amount sodium acetylide in pyridine, and heated for 30 min to 50°. The mixture was then distilled until the boiling point reached 105–110°. The fractions collected were dissolved in xylene, washed with 2% hydrochloric acid, dried with sodium sulfate, filtered, and distilled at normal pressure, b.p. 51–52° (760 mm). The yields varied between 50–70%.

The preparation of triphenylethynylgermane has been reported[13]. It can also be prepared in good yield by the method described above.

(1) *(Triphenylsilyl)(triphenylgermyl)acetylene*, $(C_6H_5)_3SiC{\equiv}CGe(C_6H_5)_3$, *(II)*

Freshly distilled diethylamine, 1.5 g (20 mmoles), in 15 ml of ether was added to a solution of 20 mmoles of butyllithium in 25 ml of hexane/ether at −78°. Triphenylchlorogermane, 6.8 g (20 mmoles), dissolved in 75 ml of ether was added slowly at room temperature. The mixture was heated at reflux for 90 min, the lithium chloride removed by filtration, and the filtrate evaporated in vacuum. The residue, crude triphenyl(diethylamino)germane, was dissolved in 20 ml of THF, added to a suspension of 0.96 g (20 mmoles) of sodium acetylide, and the mixture heated at reflux for 20 min. Triphenylchlorosilane, 5.9 g (20 mmoles), dissolved in 50 ml of THF was then added to the hot solution. After ten minutes of refluxing the mixture was cooled and clarified by filtration. The solvent was evaporated in vacuum, and the residue was recrystallized from ligroin (b.p. 110–120°) with decolorizing charcoal to give 6.5 g of a crude product, m.p. 143–200°. This substance was extracted with cold benzene and the solvent evaporated. The soluble residue was recrystallized twice from ligroin to yield a small amount of (triphenylsilyl)(triphenylgermyl)-acetylene, m.p. 152–153°.

The benzene-insoluble portion (approximately one-third of the crude yield) was recrystallized from ligroin to give a crystalline material, m.p. 200–205°. The IR spectrum of this product suggested that it was a mixture of siloxanes (absorption at $\sim 1080\ cm^{-1}$) and germoxanes (absorption at $\sim 860\ cm^{-1}$). It was probably formed by hydrolysis of the starting materials, and could not readily be further separated.

(2) *Synthesis of (triphenylsilyl)(triphenylgermyl)acetylene via an alternate method (eqns. 4, 4a and 4b)*

To a stirred suspension of 5.4 g (10 mmoles) of bis(triphenylsilyl)acetylene in 35 ml of anhydrous ether was added 7.4 ml of a 1.35 *M* solution of n-butyllithium in hexane over a 10-min period. The mixture turned slightly yellow, and was stirred for 2 h at room temperature. A solution of 3.8 g (10 mmoles) of triphenylbromogermane in 40 ml of THF was added, and the mixture stirred for another hour. The lithium salts were removed by washing with 100 ml of 2% hydrochloric acid in three portions, and 50 ml water. The organic layer was separated, dried with anhydrous magnesium sulfate, filtered, and evaporated in vacuum. The solid that remained (*ca.* 5.5 g) was extracted with 100 ml ethanol for one hour at room temperature and filtered. Butyltriphenylsilane, 1.2 g, m.p. 85° (lit[14]. m.p. 86°) was isolated from the alcoholic solution. The alcohol-insoluble part was recrystallized twice from ligroin to yield 2.5 g (42%) (triphenylsilyl)(triphenylgermyl)acetylene, m.p. 151°.

(3) *(Triphenylsilyl)(triphenylstannyl)acetylene*, $(C_6H_5)_3SiC{\equiv}CSn(C_6H_5)_3$, *(III)*

(*a*) *Direct synthesis.* A solution of 7.2 g (17 mmoles) of triphenyl(diethylamino)stannane in 25 ml of THF was added to a suspension of 0.8 g (17 mmoles) of sodium acetylide in 25 ml of THF.

A solution of 5 g (17 mmoles) of triphenylchlorosilane in 30 ml of THF was added dropwise to the mixture under reflux, and it was allowed to cool after about 5 min. The filtered solution was evaporated under vacuum, and the residue was crystallized twice from ligroin with decolorizing charcoal. The yield of (triphenylsilyl)(triphenylstannyl)acetylene was 6.7 g (68%), m.p. 124–126°.

(*b*) *Synthesis via (triphenylstannyl)ethynylsodium.* After reaction of the sodium acetylide with triphenyl(diethylamino)stannane in a procedure similar to that of (3*a*) the mixture was filtered in an inert atmosphere. Removal of the solvent under vacuum gave the sodium derivative, a solid which could be kept only in an inert atmosphere. Neutral equivalent calculated for $C_{20}H_{15}NaSn$: 397.0; found 386.6. Treatment of the sodium derivative with triphenylchlorosilane in THF as before gave (triphenylsilyl)(triphenylstannyl)acetylene in good yield, and identical with the previously obtained sample.

(4) *(Triphenylsilyl)(triphenylplumbyl)acetylene*, $(C_6H_5)_3SiC{\equiv}CPb(C_6H_5)_3$, *(IV)*

(*a*) *Direct synthesis.* This compound was prepared in a manner similar to (triphenylsilyl)(triphenylstannyl)acetylene (3*a*) but without isolation of the aminoplumbane. After two recrystallizations from ligroin(triphenylsilyl)(triphenylplumbyl)acetylene, 8.5 g (59%), m.p. 128–129°, was obtained.

(*b*) *Synthesis via (triphenylplumbyl)ethynylsodium.* This compound was prepared by a procedure similar to that of (3*b*). It was a solid that could be kept only in an inert atmosphere. Treatment of the sodium derivative with triphenylchlorosilane gave (triphenylsilyl)(triphenylplumbyl)acetylene in good yields.

(5) *(Triphenylgermyl)(triphenylstannyl)acetylene*, $(C_6H_5)_3GeC{\equiv}CSn(C_6H_5)_3$, *(VI)*

Method (*a*). A solution of 23.1 g (54.5 mmoles) of triphenyl(diethylamino)stannane in 50 ml of THF was added at room temperature to a suspension of 2.6 g (54.5 mmoles) of sodium acetylide. The reaction mixture was heated under reflux for 20 min, after which time 54.5 mmoles of triphenylchlorogermane dissolved in 70 ml of THF added. After 25 minutes of reflux (triphenylgermyl)(triphenylstannyl)-

acetylene was obtained in 87% yield, m.p. 149°, by the same procedure as before.

Method (*b*). Triphenylethynylgermane, 6.3 g (19.3 mmoles), was dissolved in ether and added to a solution of 8.1 g (19.3 mmoles) of triphenyl(diethylamino)-stannane in ether and stirred for 30 min at room temperature. After removal of the solvent in vacuum, the solid residue was recrystallized three times from ligroin to give 9.6 g (64%) of compound (VI).

(6) (*Triphenylgermyl*)(*triphenylplumbyl*)*acetylene*, $(C_6H_5)_3GeC{\equiv}CPb(C_6H_5)_3$, (*VII*)

The compound was prepared in the same manner as described under (4) without isolating the aminoplumbane. The yield of (triphenylgermyl)(triphenylplumbyl)-acetylene, m.p. 134–135°, was 8.5 g (58%), based on 19 mmoles of starting materials.

(7) (*Triphenylstannyl*)(*triphenylplumbyl*)*acetylene*, $(C_6H_5)_3SnC{\equiv}CPb(C_6H_5)_3$, (*IX*)

The preparation followed the method outlined under (4). The yield of (triphenylstannyl)(triphenylplumbyl)acetylene (IX), m.p. 143–145, was 5.9 g (56%) starting with 6.1 g (14 mmoles) triphenyllead chloride.

(8) (*Trimethylgermyl*)(*trimethylstannyl*)*acetylene*, $(CH_3)_3GeC{\equiv}CSn(CH_3)_3$, (*XIII*)

A suspension of 2.4 g (50 mmoles) of sodium acetylide in 60 ml of THF was added to a solution of 50 mmoles of trimethyl(diethylamino)stannane in ether under reflux. Trimethylchlorogermane, 7.67 g (50 mmoles), was added after 30 min. After the mixture had been heated at reflux for 3 h it was filtered and the solvent evaporated in vacuum. The vacuum distillation of the residue yielded 6.3 g (40%) of (trimethylgermyl)(trimethylstannyl)acetylene (XIII), b.p. 47° (1 mm), m.p. 41–44°.

(9) (*Trimethylsilyl*)(*trimethylstannyl*)*acetylene*, $(CH_3)_3SiC{\equiv}CSn(CH_3)_3$, (*XII*)

A solution of 50 mmoles of trimethyl(diethylamino)stannane in 100 ml of ether was added to 5 g (50 mmoles) of trimethylethynylsilane in 20 ml of ether. The mixture was stirred for 30 min at room temperature. After removal of the solvent and free amine the residue was distilled at room temperature (~25°) and 1 mm to give 8.9 g (68%) of (trimethylsilyl)(trimethylstannyl)acetylene (XII), m.p. 41–44°.

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SUMMARY

A series of organometallic acetylenes has been prepared which contain two different organometallic moieties from the Group IV elements. These compounds were synthesized via a convenient new route starting with the corresponding organometalamino compound, organometallic halide, and sodium acetylide.

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