ORGANOMETALLIC ACETYLENES OF THE MAIN GROUPS III–V

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CONTENTS

I. INTRODUCTION

The subject of this review article is organometallic-substituted acetylenes which contain the elements of the third, fourth, and fifth main groups where an alkynyl group or triple-bonded carbon atom is attached directly adjacent to the metal atom. Organometallic compounds containing acetylenic groupings further removed from the central metal atom are not reported in this paper. The lesser known polyacetylenic organometallic compounds are also reviewed consistent with the basic premise that at least one acetylenic grouping be located adjacent to the central metal atom. No prior review of the organometallic acetylides of the group III–V elements has been published.

Although one of the first organometallic alkynyl compounds of the above-mentioned elements was reported as early as 1923 (241), most of the research has been conducted within the last 15 years. This development parallels the investigations of the third, fourth, and fifth group elements containing vinyl compounds which also have been reviewed recently (256). The methods employed for the preparation of these two classes of compounds are very similar; however, as might be expected, their physical and chemical properties often differ considerably. Thus, triethynylboron and triethynylaluminum so far have been isolated only in their complexed form, whereas the trivinyl compounds of these two elements are known in their free form. The tetravinyl compounds of groups IV and V are distillable liquids; the corresponding tetraethynyl compounds are crystalline solids. Tetraethynyllead and triethynylbismuth have not yet been prepared. Comparatively, the chemistry of the vinyl compounds has been the subject of many varied types of investigations, whereas most of the chemistry on alkynyl compounds has been limited to that of the more preparative type.

A large number of the publications in this field are of Russian origin. In this review, if the corresponding translation was available, the page number was put in parenthesis after the original reference. In general, patents are only referred to if the compounds mentioned are described and identified or if a reaction is described in detail. This review includes all references through the 1965 *Chemical Abstracts*.

A. GENERAL PREPARATIVE METHODS

The syntheses of group III–V organometallic alkynes are accomplished most frequently by one of two methods: (1) the reaction of alkali acetylides with metal or organometallic halides, and (2) the corresponding reaction of acetylenic Grignard compounds with these same halides. Almost every compound listed in this review could be prepared by one of these two methods by selection of the proper conditions. There are, however, a number of other synthetic routes which are less flexible and therefore much more specific and are applicable only to certain elements of these three main groups. These latter methods will be discussed in some detail at the beginning of each section dealing with the three main groups. The methods of synthesis referred to in the tables are described in section IIIA1–6. The preparation of alkali acetylides and acetylenic Grignard reagents has been reviewed earlier (257).

B. PRECAUTIONS

In general, acetylene and acetylenic compounds are potentially hazardous. It is therefore necessary to consider the proper precautions which should be taken while working with such compounds (68).

1. *Acetylenic Starting Materials*

Information on the proper techniques for the safe handling of acetylene is amply available (127, 150). It should be kept in mind that free acetylene is often generated during reactions as a result of metalation or decomposition reactions. If low-boiling acetylenic compounds are expected, distillation into a condensing trap is frequently applied. The use of liquid air or liquid nitrogen, however, can result in the condensation of acetylene which, as a liquid, is highly explosive (127).

The temperature of the condensing bath should be above the boiling point of acetylene to avoid serious accidents. Of the halogen acetylenes, iodoacetylenes in particular should be handled with great caution (150). Monosodium acetylide can be handled with reasonable safety, whereas disodium acetylide reacts almost explosively with water. The preparation of alkali haloacetylides has been reported recently (230–234) and these substances are very explosive. Their isolation from solution is not advisable. Many heavy metal acetylides are explosive (127). Acetylenic Grignard compounds until recently had not been considered to be overly hazardous. A serious explosion took place in early 1966 during the preparation of an acetylenic Grignard solution *via* an alkylmagnesium iodide (258).

2. *Organometallic Acetylene Compounds*

Some of the ethynylaluminum complexes have been reported to be explosive under certain conditions (27). Tetrakischloroethynylsilane, $Si(C{\equiv}CCl)_4$, which is reported to detonate on friction, is stated to be thermally stable (231). Tetraethynylgermane, tetraethynyltin, and alkynyllead compounds have been reported to explode on rapid heating (29, 78, 249). Tetraethynylgermane is also reported to be sensitive to friction (117). A highly explosive material was also obtained from bis(triethyltin)acetylene and tin tetrachloride (8). The triethynyl compounds of the fifth main group elements are very explosive on strong friction (237). Triethynylphosphine gradually turns black on standing. On one occasion such a black product exploded spontaneously. The fact that many of the compounds prepared have not been reported to be explosive does not necessarily mean that they are harmless and until completely characterized they should not be considered to be other than potentially hazardous. In addition to the explosive properties of these compounds, in general, it should not be overlooked that many organometallic compounds of the three main groups in question are highly toxic. Organothallium compounds, alkyl compounds of tin and lead, and compounds of the fifth main group, particularly the volatile members, should be treated with particular caution. Virtually nothing is known as yet about the toxicity of organometallic alkynyl compounds; however, until information is obtained to the contrary, it can be assumed that the toxicity will be at least of the same order of magnitude as the parent compounds.

C. SPECTROSCOPY OF ORGANOMETALLIC ACETYLIDES

Detailed studies of the vibrational spectrum exist only for the following ethynylsilanes: $H_3SiC{\equiv}CH$ (34), $(CH_3)_3SiC{\equiv}CH$ (22), $(CH_3)_3SiC{\equiv}CBr$, $(CH_3)_3SiC{\equiv}CI$ (23), and $(CH_3)_2Si(C{\equiv}CH)_2$ (24). The Raman spectrum of some symmetrically substituted acetylenes is also reported: $Cl_3SiC{\equiv}CSiCl_3$, $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, and $(CH_3O)_3SiC{\equiv}CSi(OCH_3)_3$ (91).

The $C{\equiv}C$ stretching vibration of organic substituted alkynes is observed at 2120 cm^{-1}. This band shifts in all organometallic ethynyl compounds to lower frequencies and can be found between 2000 and 2060 cm^{-1}. In the case of $(CH_3)_3SiC{\equiv}CH$ it has been calculated that this shift is caused partially by dative π bonding (239). With decreasing electronegativity of the elements from silicon to lead the effect of this interaction becomes less significant and the mass of metal atom together with the force constants of the metal–carbon bonds are considered to be the predominant causes for the frequency shifts (42, 228, 239).

The intensity of the $C{\equiv}C$ stretching vibration increases considerably with the number of ethynyl groups attached to the metal atom. This fact has been established for compounds of the type $R_{4-n}Si(C{\equiv}CH)_n$ and can be used to determine the number of acetylenic bonds in these compounds (204). For alkynylsilanes of the type $R_3SiC{\equiv}CC(CH_3)_2R'$ it has been found that the change of R' does not influence the position of the absorption bands. The integral intensities, however, depend on the organic substituent on the silicon atom, R' and R (209). The $C{\equiv}C$ and ${\equiv}CH$ stretching vibrations of the alkynyl compounds are listed in many papers. Only a few reports discuss nmr and ultraviolet data in detail although the following may be useful: Al, nmr (30); Ge, infrared (115); Sn, infrared, nmr, and ultraviolet (103); Pb, infrared, nmr, and ultraviolet (109); P, infrared, nmr, and ultraviolet (25); and As, infrared, and nmr (9).

The C≡C and ≡CH stretching vibrations of tri- and tetraethynyl compounds are reported in Table I.

TABLE I

Compound	Str, cm^{-1} C≡C	≡CH	Ref
$B(C{\equiv}CH)_3\cdot C_5H_5N$	2060		6
$Al(C{\equiv}CH)_3\cdot C_4H_8O_2$	2000	3320	27
$Si(C{\equiv}CH)_4$	2062	3306	29
$Ge(C{\equiv}CH)_4$	2059	3303	29
$Sn(C{\equiv}CH)_4$	2050	3200	78
$P(C{\equiv}CH)_3$	2054	3291	237
$As(C{\equiv}CH)_3$	2045	3291	237
$Sb(C{\equiv}CH)_3$	2025	3291	237

Organometallic diacetylides and some triacetylides are reported to have two bands in the 2050–2200-cm^{-1} region. The bands are approximately 50–100 cm^{-1} apart and the lower frequency can probably be assigned to MC≡C stretch.

II. ALKYNYL COMPOUNDS OF THE THIRD MAIN GROUP ELEMENTS

Surprisingly little has been reported about the synthesis and chemistry of the group III acetylenic compounds. Indium and thallium derivatives are unknown and only one report has appeared in the literature describing alkynylgallium compounds (35).

A. ALKYNYLBORON COMPOUNDS

Some of the work done in this field has been considered in a recent Russian review article on unsaturated organoboron compounds (229).

1. *Preparative Methods*

Two methods are used for the synthesis of alkynylboranes: (a) reaction of boron halides (preferably boron trifluoride) or organoboron halides (RBX_2, R_2BX) with alkali acetylides or acetylenic Grignard compounds; (b) reaction of alkyl aryl borates $B(OR)_3$ with acetylenic Grignard compounds. Usually methods a and b are carried out in the presence of a complexing agent, most frequently pyridine, since the substances prepared are more (or sometimes only) stable in the complexed form.

2. *Trialkynylboranes, $B(C{\equiv}CR)_3$ (Table II)*

Experiments designed to prepare pure trialkynylboranes, under a variety of conditions, led only to polymeric products. Trialkynylboranes are, however, stable in the form of coordination complexes with amines, and ethers (6). Triethynylborane–pyridine and tris(phenylethynyl)borane–pyridine were obtained by the reaction of a boron trifluoride–pyridine complex with sodium acetylide or phenylethynylsodium in pyridine. An attempt to synthesize triethynylborane from trimethyl borate and sodium acetylide resulted in the formation of sodium ethynyltrimethoxyborate, $NaB(OCH_3)_3C{\equiv}CH$, a complex soluble in tetrahydrofuran (6). The tris(phenylethynyl)borane–tetrahydrofuran complex can be prepared from sodium or ammonium tetra(phenylethynyl)borate by adding to a tetrahydrofuran solution an ether solution of hydrogen chloride at −5°.

TABLE II

TRIALKYNYLBORANES, $B(C{\equiv}CR)_3$

Compound	Mp, °C	Yield, %	Ref
$B(C{\equiv}CH)_3\cdot C_5H_5N$	153	...	6
$B(C{\equiv}CH)_3\cdot (C_2H_5)_2NH$	105–108	75	6
$B(C{\equiv}CH)_3\cdot (CH_3)_3N$	219	...	6
$B(C{\equiv}CC_6H_5)_3\cdot C_5H_5N$	210–230, dec	...	6, 94
$BC{\equiv}CC_6H_5)_3\cdot (CH_3)_2NH$	210–220, dec	...	94
$B(C{\equiv}CC_6H_5)_3\cdot NH_3$	210–220, dec	...	94
$B(C{\equiv}CC_6H_5)_3\cdot THF$	85–110, polymerizes	...	94

$$Na[B(C{\equiv}CC_6H_5)_4] + HCl \xrightarrow{THF} B(C{\equiv}CC_6H_5)_3\cdot THF + C_6H_5{\equiv}CH + NaCl$$

3. *Dialkynylorganoboranes, $RB(C{\equiv}CR)_2$ (Table III)*

Four compounds of this type have been prepared thus far, only one of which was isolated in an uncomplexed form. It is interesting to note that tris(phenylethynyl)borane exists only in complexed form, whereas phenyl(diphenylethynyl)borane can be isolated as a crystalline substance melting at 84° (100). Besides their melting points and some more or less general infrared assignments, little is known about the physical and chemical properties of these compounds. This is also true for the next group of acetylenic boranes.

TABLE III

DIALKYNYLORGANOBORANES, $RB(C{\equiv}CR)_2$

Compound	Mp, °C	Yield, %	Ref
$C_6H_5B(C{\equiv}CC_6H_5)_2$	84–85	...	100
$C_6H_5B(C{\equiv}CH)_2\cdot C_5H_5N$	120	15	47
$C_6H_5B(C{\equiv}CCH_3)_2\cdot C_5H_5N$	158	39	47
$C_6H_5B(C{\equiv}CC_6H_5)_2\cdot C_5H_5N$	139	46	47

4. *Monoalkynylorganoboranes, $R_2BC{\equiv}CR$ (Table IV)*

The majority of compounds reported in this section are pyridine coordination complexes of diarylalkynylboranes. Diphenyl(phenylethynyl)borane is the only one which has been prepared as an uncomplexed compound (100). Only one dialkylalkynylborane, $Bu_2BC{\equiv}CC(CH_3){=}CH_2$, is known. This compound ignites spontaneously in air, exhibiting the same sensitivity toward oxygen as most alkylboranes (132). Several dibutylalkynyl borates have been synthesized and the chemistry of dibutylacetylene borate has been studied in greater detail than of any other alkynylboron compound. It is interesting to note that free radical species may be added to the carbon–carbon triple bond

TABLE IV

MONOALKYNYLORGANOBORANES

A. $R_2BC{\equiv}CR'\cdot$Pyridine

Compound	Mp, °C	Yield, %	Ref
$(C_6H_5)_2BC{\equiv}CH\cdot pyr$	150	41	223
$(C_6H_5)_2BC{\equiv}CCH_3\cdot pyr$	170	48	223
$(C_6H_5)_2BC{\equiv}CC_6H_5\cdot pyr$	158	68	223
$(C_6H_5)_2BC{\equiv}CC_6H_4Br\text{-}p\cdot pyr$	165	77	223
$(C_6H_5)_2BC{\equiv}CCH_2C_{14}H_9\cdot pyr^a$	205	48	223
$(o\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CH\cdot pyr$	137	27	47
$(m\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CH\cdot pyr$	117	32	47
$(p\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CH\cdot pyr$	128	50	47
$(p\text{-}CH_3C_6H_4)(p\text{-}CH_3OC_6H_4)BC{\equiv}CH\cdot pyr$	153	38	47
$(o\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CCH_3\cdot pyr$	138	20	47
$(m\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CCH_3\cdot pyr$	145	38	47
$(p\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CCH_3\cdot pyr$	138	47	47
$(p\text{-}CH_3C_6H_4)(p\text{-}CH_3OC_6H_4)BC{\equiv}CCH_3\cdot pyr$	160	55	47
$(o\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CC_6H_5\cdot pyr$	141	50	47
$(m\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CC_6H_5\cdot pyr$	125	89	47
$(p\text{-}CH_3C_6H_4)(C_6H_5)BC{\equiv}CC_6H_5\cdot pyr$	145	63	47
$(p\text{-}CH_3C_6H_4)(p\text{-}CH_3OC_6H_4)BC{\equiv}CC_6H_5\cdot pyr$	160	46	47
$(C_6H_5)_2BC{\equiv}CCH{=}CH_2\cdot pyr$	130	41	47
$(C_6H_5)_2BC{\equiv}CC(CH_3){=}CH_2\cdot pyr$	130	70	47
$(C_6H_5)_2BC{\equiv}CC(C_5H_7){=}CH_2\cdot pyr^b$	163	60	47
$(C_6H_5)_2BC{\equiv}CC(C_6H_9){=}CH_2\cdot pyr^c$	139	70	47
$(C_6H_5)_2BC{\equiv}CC(C_9H_{15}){=}CH_2\cdot pyr^d$	154	60	47
$(C_6H_5)_2BC{\equiv}CSi(CH_3)_3\cdot pyr$	130	41	223
$(C_6H_5)_2BC{\equiv}CCH_2Si(CH_3)_3\cdot pyr$	178	55	223
$(C_6H_5)_2BC{\equiv}CSC_2H_5\cdot pyr$	158	44	223
$(C_6H_5)BC{\equiv}CB(C_6H_5)_2\cdot pyr$	170	27	223

B. $R_2BC{\equiv}CR$

Compound	Mp, °C	Bp (mm)	n_D^{20}	d_4^{20}	Yield, %	Ref
$(C_6H_5)_2BC{\equiv}CC_6H_5$	108–110		...	...	...	100
$(C_4H_9O)(C_6H_5)BC{\equiv}CH$	Dec on distillation		...	...	...	113
$(C_4H_9O)(C_8H_9)BC{\equiv}CH^e$		75 (0.1)	1.5095^f	...	...	113
$(C_4H_9)_2BC{\equiv}CC(CH_3){=}CH_2$		22–25 (0.1)	1.4509	...	...	132
$(C_4H_9O)_2BC{\equiv}CH$		30–32 (0.3)	1.4180^g	...	58–63	111, 112
$(C_4H_9O)_2BC{\equiv}CCH_3$		103 (10)	1.4212	0.8582	...	250
$(C_4H_9O)_2BC{\equiv}CC_4H_9\text{-}n$		85–90 (0.1)	1.4357^g	...	39	111, 112
$(C_4H_9O)_2BC{\equiv}CCH{=}CH_2$		109–110 (10)	1.4370	0.8614	...	250

[a] Anthranyl. [b] Cyclopentenyl. [c] Cyclohexenyl. [d] 2-Methyl-6,6-dimethylcyclohexenyl. [e] 2,5-Dimethylphenyl. [f] 24.3°. [g] 26°.

without cleavage of the carbon–boron bond (112). The addition of (a) bromotrichloromethane to dibutylacetylene borate yields dibutyl-3,3,3-trichlorobromopropene-1 borate; (b) hydrogen bromide yields dibutyl-2,2-bromoethylene borate; and (c) bromine yields dibutyl-1,2-dibromoethylene borate. The addition reaction of thiols results in the corresponding 1:1 adducts

$$RSH + HC{\equiv}CB(OC_4H_9)_2 \longrightarrow RSCH{=}CHB(OC_4H_9)_2$$

Diels–Alder-type reactions (111) and additions of diazo compounds have also been described (112). The sensitivity of dibutylacetylene borate toward bases does not under normal circumstances allow addition of nucleophilic reagents.

5. *Bis(dialkylboron)acetylenes,* $R_2BC{\equiv}CBR_2$

The synthesis and properties of bis(dialkylboron)acetylenes are the subject of a single paper (54). They are described as thermally unstable liquids, similar in this respect to the mixed alkylboron compounds. They are, however, distillable at lower temperatures under vacuum. Hydrolysis of bis(dialkylboron)acetylenes can be achieved by shaking with water

$$R_2BC{\equiv}CBR_2 + 2HOH \longrightarrow 2R_2BOH + C_2H_2$$

Bis(dialkylboron)acetylenes, thus far prepared, ignite on contact with air. Attempts to slowly react this type of acetylene compound with oxygen and isolate bis(dialkoxyborane)acetylene as a possible intermediate were not successful. The stabilization of these acetylenic boron compounds with organic nitrogen compounds did not lead to positive results. The pyridine complex of bis(diphenylboron)acetylene was defined by another group of research workers as a solid melting at 170° (223) (Table V).

6. *Tetra(phenylethynyl)borates,* $MB(C{\equiv}CC_6H_5)_4$

The sodium, ammonium, and magnesium salts of the hypothetical tetra(phenylethynyl)boric acid,

TABLE V

BIS(DIALKYLBORON)ACETYLENES, $R_2BC{\equiv}CBR_2$

Compound	Mp, °C	Bp, °C (mm)	Ref
$(i\text{-}C_3H_7)_2BC{\equiv}CB(C_3H_7\text{-}i)_2$		55–56 (1)	54
$(n\text{-}C_3H_7)_2BC{\equiv}CB(C_3H_7\text{-}n)_2$		70–75 (1)	54
$(i\text{-}C_4H_9)_2BC{\equiv}CB(C_4H_9\text{-}i)_2$		78–79 (1)	54
$(n\text{-}C_4H_9)_2BC{\equiv}CB(C_4H_9\text{-}n)_2$		98–100 (1)	54
$(C_6H_5)_2BC{\equiv}CB(C_6H_5)_2 \cdot C_5H_5N$	170	. . .	223

$HB(C{\equiv}CC_6H_5)_4$ have been prepared and described (92–94, 155) (Table VIA).

TABLE VI

ALKYNYLBORATES, $M[B(R)_n(C{\equiv}CR')_{4-n}]$

Compound	Mp, °C	Yield, %	Ref
A. Tetra(phenylethynyl)borates, $M[B(C{\equiv}CC_6H_5)_4]$			
$Na[B(C{\equiv}CC_6H_5)_4]$	300 detonates Crystallizes with solvent of crystzn from Et_2O, H_2O, THF, CH_3OH	. .	92
$NH_4[B(C{\equiv}CC_6H_5)_4]$	160–225 dec	. .	93, 155
$Mg[B(C{\equiv}CC_6H_5)_4]_2 \cdot 6H_2O$	Soluble in boiling H_2O Removal of H_2O of crystzn results in decompn		93, 223
B. Sodium Trialkylalkynylborates, $Na[B(R_3)C{\equiv}CR']$			
$Na[B(CH_3)_3C{\equiv}CCH_3]$	163	68	14
$Na[B(CH_3)_3C{\equiv}CC_2H_5]$	166	65	14
$Na[B(CH_3)_3C{\equiv}CC_6H_5]$	146 dec	78	14
$Na[B(C_2H_5)_3C{\equiv}CCH_3]$	89	89	14
$Na[B(C_2H_5)_3C{\equiv}CC_2H_5]$	65	87	14
$Na[B(C_2H_5)_3C{\equiv}CC_6H_5]$	129	98	14
$Na[B(C_3H_7)_3C{\equiv}CCH_3]$	120	95	14
$Na[B(C_3H_7)_3C{\equiv}CC_2H_5]$	134	97	14
$Na[B(C_3H_7)_3C{\equiv}CC_6H_5]$	177	77	14

7. *Trialkylalkynylborates, $M(R_3BC{\equiv}CR')$*

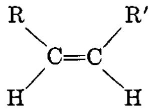
Alkali trialkylborates and substituted acetylenes yield alkali trialkylalkynylborates as follows

$$Na(R_3BH) + HC{\equiv}CR' \longrightarrow Na(R_3BC{\equiv}CR') + H_2$$

With acetylene, the disodium salt is formed, $Na_2(R_3BC{\equiv}CBR_3)$. In contrast to the reactions of the corresponding alanates, $Na(R_3AlH)$, hydrogen formation is hindered in polar solvents like ether or tetrahydrofuran. Dilution with benzene or hexane produces the salts in crystalline form. Alkali trialkylalkynylborates react with dialkychloroboranes in polar solvents to form *cis*-1,2-bis(dialkylboryl)alkenes in 70–80% yield (14)

$$Na(R_3BC{\equiv}CR') + R'_2BCl \longrightarrow R(R_2B)C{=}C(R_2B)R' + NaCl$$

Decomposition with water results in pure *cis*-alkenes.



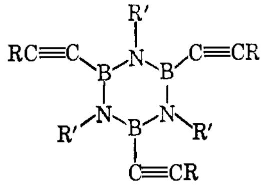
No other compounds of this type are reported (Table VIB).

8. *Alkynylborazines*

Thus far, homologs of B-triethynylborazines are the only alkynylborazines that have been prepared and characterized. These compounds have been synthesized by reacting B-trichloroborazine with alkynyl Grignard reagents. Catalytic reduction of the B-triethynylborazines using palladium black yielded the corresponding substituted ethylborazines. Hydrolysis of these ethynylborazines yielded the parent acetylene, amine, and boric acid (238) (Table VII).

TABLE VII

B-TRIETHYNYLBORAZINES



Compound	Mp, °C	Yield, %	Ref
$B_3(C{\equiv}CC_6H_5)_3N_3H_3$	139–140	64	238
$B_3(C{\equiv}CC_6H_5)_3N_3(CH_3)_3$	217–218	81	238
$B_3(C{\equiv}CC_6H_5)_3N_3(C_6H_5)_3$	240–242	83	238
$B_3(C{\equiv}CCH_3)_3N_3H_3$	100–102	24	238
$B_3(C{\equiv}CCH_3)_3N_3(CH_3)_3$	187–189	82	238
$B_3(C{\equiv}CCH_3)_3N_3(C_6H_5)_3$	245–246	38	238

B. ALKYNYLALUMINUM COMPOUNDS

There is even less information on acetylenic aluminum compounds available in the literature than on boron compounds. The patents published in this field are concerned with the preparation of acetylenic aluminum compounds by more or less conventional methods and do not reveal much of interest about the properties of these compounds. In one patent the possible use of alkynylaluminum compounds as polymerization catalysts is indicated (128).

1. *Preparative Methods*

The reaction of aluminum halides and organoaluminum halides with sodium acetylides is generally used for the preparation of alkynylaluminum compounds. Alkynylaluminum compounds can also be obtained from the reaction of trialkyl- or triarylaluminum with the acidic hydrogen of phenylacetylene or monoalkylacetylenes

$$RC{\equiv}CH + R'_3Al \longrightarrow RC{\equiv}CAlR'_2 + R'H$$

This metalation reaction was first observed in 1962 (132) and more recently has been reported in some detail (124, 125).

2. Trialkynylaluminum Compounds, Al(C≡CR)₃ (Table VIII)

Coordination complexes of triethynylaluminum with tetrahydrofuran, dioxane, trimethylamine, and pyridine have been prepared (27). Some of these complexes can be sublimed although suitable precautions should be taken as explosions are possible. It is not known whether the preparation of uncomplexed triethynylaluminum has been attempted. The tris(propynyl)-, tris(hexynyl)-, and tris(phenylethynyl)aluminum compounds are also known in their complexed form. Tris(hexynyl)aluminum could not be stabilized with pyridine (27); however, the corresponding dioxane complex is a solid melting at 62°.

TABLE VIII
TRIALKYNYLALUMINUM COMPOUNDS, $Al(C{\equiv}CR)_3$

Compound	Mp, °C	Yield, %	Ref
$Al(C{\equiv}CH)_3 \cdot$dioxane	165–170 dec 60–80 (0.01 mm) subl	67.6	27
$Al(C{\equiv}CH)_3 \cdot$THF	No data	Quant	27
$Al(C{\equiv}CH)_3 \cdot N(CH_3)_3$	144–146 dec 70 (0.01) subl (caution)	43	27
$Al(C{\equiv}CH)_3 \cdot 2$pyr	No data	...	27
$Al(C{\equiv}CCH_3)_3 \cdot$THF	85–95 (0.01) subl with dec	72.5	27
$Al(C{\equiv}CC_4H_9\text{-}n)_3 \cdot$dioxane	62–63	68	27
$Al(C{\equiv}CC_6H_5)_3 \cdot N(CH_3)_3$	176–178	63	27

3. Complex Alkali–Aluminum Acetylides, MAl(C≡CR)₄ (Table IX)

A number of these alkali–aluminum acetylide complexes have been reported. Alkali aluminum hydrides, for example, react with acetylenes to form alkali aluminum alkynyl compounds of varying composition depending probably on the reaction temperature. Sodium aluminum hydride and *n*-hexyne-1 in refluxing xylene react to form sodium tetrakis-*n*-hexynyl-1-aluminum.

TABLE IX
ALKALI ALUMINUM ACETYLIDES, $M[Al(R_n)(C{\equiv}CR)_{4-n}]$

Compound	Mp, °C	Yield, %	Ref
$Li[Al(C{\equiv}CH)_4] \cdot$THF		..	27
$Na[Al(C{\equiv}CH)_4] \cdot$dioxane		..	27
$Li[Al(C{\equiv}CC_6H_5]_4$		..	27
$Na[Al(C{\equiv}CC_4H_9\text{-}n)_4]$	190	81	247
$Na[Al(C{\equiv}CC_6H_5)_4]$	No data	..	247
$Na[H_2Al(C{\equiv}CC_4H_9\text{-}n)_2]$	...	60	247
$Na[H_3AlC{\equiv}CC_4H_9\text{-}n]$	175–180 dec	57	247
$Na[(CH_3)_2Al(C{\equiv}CC_6H_5)_2] \cdot$THF	190–191	60	247
$Na[C_2H_5Al(C{\equiv}CC_6H_5)_3]$	173–174	58	247
$Na[(C_2H_5)_2Al(C{\equiv}CC_6H_5)_2]$	123–124	90	247
$Na[(CH_3)_2CHCH_2Al(C{\equiv}CC_6H_5)_3]$	108–110	..	247
$Na\{[(CH_3)_2CHCH_2]_3AlC{\equiv}CC_6H_5\}$	120–125	..	247

$$NaAlH_4 + HC{\equiv}CC_4H_9 \longrightarrow NaAl(C{\equiv}CC_4H_9)_4 \quad (81\% \text{ yield})$$

In refluxing tetrahydrofuran only one hydrogen atom is replaced by a hexynyl group resulting in the formation of $NaAlH_3(C{\equiv}CC_4H_9)$, 57% yield. A redistribution reaction occurs between sodium aluminum hydride and sodium tetrahexynylaluminum in refluxing xylene

$$NaAlH_4 + NaAl(C{\equiv}CC_4H_9)_4 \longrightarrow NaAlH_2(C{\equiv}C_4H_9)_2 \quad (60\% \text{ yield})$$

Sodium tetraalkylaluminum compounds react with acetylenes to yield mixed complexes (246)

$$NaAl(CH_3)_4 \cdot C_4H_8O + C_6H_5C{\equiv}CH \xrightarrow{\text{refluxing xylene}} NaAl(CH_3)_2(C{\equiv}CC_6H_5)_2 \cdot C_4H_8O$$

$$NaAl(C_2H_5)_4 + C_6H_5C{\equiv}CH \xrightarrow[200°]{\text{tetrahydronaphthalene}} NaAlC_2H_5(C{\equiv}CC_6H_5)_3$$

These complex acetylides react with carbonyl compounds to form acetylenic alcohols in good yields (245).

$$MAl(C{\equiv}CR)_4 + R_2C{=}O \longrightarrow R_2C(OH)C{\equiv}CR$$

With carbon dioxide, carboxylic acids can be obtained.

4. Diorganoacetylides of Aluminum, R₂AlC≡CR (Table X)

Dimethyl(phenylethynyl)aluminum is a crystalline solid, melting at 100–106° with decomposition. The corresponding diethyl compound is a thermally unstable liquid which ignites in contact with air. The other diethyl(alkynyl)aluminum compounds are also sensitive to oxidation but can be distilled under high vacuum (30). In a similar manner to the complex aluminum acetylides, diethyl(alkynyl)aluminum compounds react with carbonyl groups and can therefore be used to synthesize acetylenic alcohols

$$R_2C{=}O \xrightarrow{(C_2H_5)_2AlC{\equiv}CR'} R_2C(OH)C{\equiv}CR'$$

TABLE X
MONOALKYNYLALUMINUM COMPOUNDS, $R_2AlC{\equiv}CR$

Compound	Mp, °C	Bp, °C (mm)	Yield, %	Ref
$(CH_3)_2AlC{\equiv}CC_6H_5$	100–106		73	125
$(CH_3)_2AlC{\equiv}CC_{10}H_7$[a]	190 dec		...	124
$(C_2H_5)_2AlC{\equiv}CCH_3$		50 (0.001)	50	5, 13, 20
$(C_2H_5)_2AlC{\equiv}CC_2H_5$		76 (0.07)	45–90	30, 147, 242, 243
$(C_2H_5)_2AlC{\equiv}CC(CH_3){=}CH_2$		82–85 (10^{-3})	35	30
$(C_2H_5)_2AlC{\equiv}CC_6H_5$		80–82 (10^{-3}) dec	12	30
$(C_2H_5)_2AlC{\equiv}CC_6H_9$[b]		73–77 (10^{-3})	18	30
$(C_5H_5)_2AlC{\equiv}CC_4H_9\text{-}n$	86–87	dec	...	36
$(C_6H_5)_2AlC{\equiv}CC_6H_5$	142–144		86	36, 125

[a] $C_{10}H_7$ = naphthyl. [b] C_6H_9 = cylcohexenyl.

C. ALKYNYLGALLIUM COMPOUNDS

Triethylgallium undergoes metalation reactions with acetylenes

$$Ga(C_2H_5)_3 + HC{\equiv}CR' \longrightarrow Ga(C_2H_5)_2C{\equiv}CR$$

Three gallium compounds have been obtained by this method: (a) diethylethynylgallium, $(C_2H_5)_2GaC{\equiv}CH$; (b) diethyl(1-hexynyl)gallium, $(C_2H_5)_2GaC{\equiv}CC_4H_9$; and (c) tris(1-hexynyl)gallium, $Ga(C{\equiv}CC_4H_9)_3$. All three of these compounds are unstable in air and have been identified mainly by indirect methods (35).

III. ALKYNYL COMPOUNDS OF THE FOURTH MAIN GROUP ELEMENTS

A large number of the group IV containing metal organic alkynyl compounds has been prepared. Of these, more than 60% are silicon derivatives.

A. PREPARATIVE METHODS

1. *Synthesis with Alkali Acetylides*

a. In Liquid Ammonia

Although liquid ammonia is an excellent solvent for sodium acetylides, its use is limited to the synthesis of tin- and lead-containing organic acetylenes. Silicon and germanium halides, in general, undergo a fast ammonolysis and thus are not capable of forming acetylenic derivatives in this medium. The only products obtained from the reaction of sodium acetylide and organotin and organolead halides were disubstituted acetylenes of the type $R_3MC{\equiv}CMR_3$ (8). Based on this result and a number of experimental observations, a metalation reaction as explanation was excluded and the formation of an intermediate complex, $Na[R_3M(C{\equiv}CH)_2]$, was suggested which in turn decomposes upon removal of the ammonia at room temperature (8). Two more recent papers report the successful preparation of triphenylethynyltin and triphenylethynyllead as a result of the rapid addition of the corresponding metal organic iodides to a liquid ammonia–sodium acetylide solution. Yields of 70 and 50% were reported using a reaction time of but a few minutes (103, 109). The corresponding diacetylenes were prepared in an analogous manner. Disubstituted products were also isolated from these reactions. The authors of the foregoing papers prefer to explain the formation of these compounds by means of a mechanism utilizing fast metalation of the monosubstituted acetylenes. Disodium diacetylide and disodium triacetylide were applied to yield the corresponding disubstituted acetylenes. One author reports the reaction of sodium chloroacetylide with triphenyltin chloride (230)

$$(C_6H_5)_3SnCl + NaC{\equiv}CCl \longrightarrow (C_6H_5)_3SnC{\equiv}CCl \quad (80\%\ \text{yield})$$

Sodium acetylides and sodium diacetylides also react with dialkyltin, which when followed by alkylation yield mixed alkylalkynyltin derivatives (254)

$$(C_2H_5)_2Sn + NaC{\equiv}CR \longrightarrow (C_2H_5)_2SnNa(C{\equiv}CR)$$

$$(C_2H_5)_2SnNa(C{\equiv}CR) + C_2H_5Br \longrightarrow (C_2H_5)_3SnC{\equiv}CR + NaBr$$

b. In Organic Solvents

The reaction of sodium acetylides in organic solvents is more versatile (151). The tetrachlorides of silicon and germanium as well as the organosubstituted chlorosilanes do not react with sodium acetylide in benzene, diethyl ether, or a mixture of both (70). This difficulty has been overcome by using pyridine (19) and tetrahydrofuran (29). Lithium chloroacetylide when reacted with tetrachlorosilane yielded tetrakischloroethynylsilane (231)

$$SiCl_4 + 4LiC{\equiv}CCl \longrightarrow Si(C{\equiv}CCl)_4 + 4LiCl$$

Complexes of sodium acetylide with boron or aluminum organic compounds are reported to react readily with organochlorosilanes (79, 80). These complexes are soluble in many organic solvents and it is assumed that the reactivity of sodium acetylide toward chlorosilanes is simply enhanced by increased solubility. This same patent, however, claims that trimethylethynylsilane can be obtained in good yield by adding trimethylchlorosilane to a suspension of the sodium acetylide–triethylaluminum complex, $NaC{\equiv}CH \cdot Al(C_2H_5)_3$, in paraffin oil at 85°.

Another interesting modification is the use of bistrimethylsilicon sulfate in diethyl ether instead of the chloride. This method is reported to give good yields of trimethylethynylsilane (221).

The formation of higher substituted by-products has been reported in only two instances

$$(C_2H_5O)_2SiCl_2 + NaC{\equiv}CH \xrightarrow{\text{pyridine}} (C_2H_5O)_2Si(C{\equiv}CH)_2 + HC{\equiv}CSi(OC_2H_5)_2C{\equiv}CSi(OC_2H_5)_2C{\equiv}CH \quad (19)$$

$$(C_4H_9)_2GeCl_2 + NaC{\equiv}CH \xrightarrow{\text{tetrahydrofuran}} (C_4H_9)_2Ge(C{\equiv}CH)_2 + HC{\equiv}CGe(C_4H_9)_2C{\equiv}CGe(C_4H_9)_2C{\equiv}CH \quad (29)$$

The formation of the above by-products can be repressed to some extent by adding the sodium acetylide to the halide solution (19). A metalation reaction in these cases is likely but has not definitely been established. Tin halides react smoothly with sodium acetylide in diethyl ether to produce the corresponding ethynyltin derivatives, including tetraethynyltin, in high yields (78).

Alkali metal alkynyl compounds, preferably the lithium salts ($LiC{\equiv}CR$), also have been used to synthesize group IV alkynyl compounds (44, 46, 57, 64, 66, 67). Rubidium hexachloroplumbate reacts with alkynyllithium to yield tetraalkynyllead compounds (66, 67).

The interaction of trialkyltin hydroxide (R_3SnOH) or trialkyltin oxides, ($R_3SnOSnR_3$) with sodium acetylides and disodium acetylide also results in the formation of various alkynyltin compounds (205, 220).

2. Synthesis with Acetylenic Grignard Compounds

The use of acetylenic Grignard reagents, easily prepared and soluble in many organic solvents, is still the preferred method for the synthesis of organometallic alkynyl compounds. The di-Grignard of acetylene, the so-called Iotsich reagent ($BrMgC{\equiv}CMgBr$), has been known for more than 60 years (127). About 50 years after the first preparation of this compound, the reagent was applied for the first time for the synthesis of organometallic acetylene derivatives (39, 146, 137). The solubility of the di-Grignard in diethyl ether is limited, and chloroform, being a better solvent, is recommended (8). The preparation of ethynylmagnesium bromide ($HC{\equiv}CMgBr$) was difficult because of facile disproportionation into the di-Grignard. In 1956 an elegant method was published which made this reagent readily available (82). Since then many group IV ethynyl derivatives of the type $R_{4-n}M(C{\equiv}CH)_n$ have been synthesized with this reagent. Monosubstituted acetylenes readily form Grignard compounds by simply reacting ethylmagnesium bromide with the appropriate acetylene in diethyl ether. These Grignard reagents react with organometallic halides without difficulty. The use of catalytic amounts of cuprous chloride or mercuric chloride is often recommended. The use of silicon fluorides instead of chlorides is sometimes advantageous, particularly, in the case of triphenylfluorosilane (141).

Acetylenic Grignard compounds also react with polyalkylsiloxanes (88, 195, 214)

$$(R_2SiO)_x + BrMgC{\equiv}CR' \longrightarrow R_2Si(OH)C{\equiv}CR'$$

The reaction products in these cases are acetylenic silanols, whereas, similar reactions with dialkyltin oxides yield dialkynyldialkyltin compounds (208, 219)

$$R_2SnO + BrMgC{\equiv}CR' \xrightarrow{THF} R_2Sn(C{\equiv}CR')_2$$

3. Reaction of Organometallic Amines with Acetylenes

It is somewhat surprising that this reaction, which can be described as $R_mM(NR_2)_n + nHC{\equiv}CR' \rightarrow R_mM(C{\equiv}CR')_n + nHNR_2$, has only been utilized twice for the preparation of alkynyl organometallic compounds. The organometallic amines of group IV are known to be reactive toward compounds with acidic hydrogens. The silylamines, although particularly well known, have not been reacted with organoacetylenes, no alkynylsilicon compounds prepared *via* this route thus far having been reported. Tributyl(phenylethynyl) germane has been prepared by reacting tributyl(diethylamino)germane with phenylacetylene at 150° (153). Organotin amines are reported to react nearly quantitatively under mild conditions with acetylenes (100).

4. Syntheses Using Haloacetylenes

Although the organometallic alkali metal compounds of group IV are well known and relatively easy to prepare, the synthesis of trialkyl(aryl)alkynyl derivatives from the corresponding organometallic alkyl compounds and haloacetylenes has been used for only a relatively small number of tin and lead compounds (8, 102, 134, 249, 251, 252, 254, 255).

5. Syntheses of Organotin Acetylides from Organotin Oxides and Organotin Hydroxides

The reaction of organotin oxides and hydroxides with acetylenic compounds offers a simple and convenient method for the preparation of numerous alkynyltin compounds, often in very good yields. The reaction of trialkyltin hydroxides probably involves an electrophilic attack by the acetylenic hydrogen on the oxygen atom of the organotin hydroxide since the reaction rate increases with increasing acidity of the hydrocarbon (205)

$$R_3SnOH + HC{\equiv}CR' \longrightarrow R_3SnC{\equiv}CR' + H_2O$$

Trialkyltin oxides react with acetylene at 8–12 atm to give trialkyltin acetylide (205)

$$R_3SnOSnR_3 + 2HC{\equiv}CH \longrightarrow 2R_3SnC{\equiv}CH + H_2O$$

Triethyltin acetylide reacts with triethyltin oxide to yield bis(triethyltin) acetylene.

$$2(C_2H_5)_3SnC{\equiv}CH + [(C_2H_5)_3Sn]_2O \longrightarrow 2(C_2H_5)_3SnC{\equiv}CSn(C_2H_5)_3 + H_2O$$

The same reaction with triethyltin hydroxide proceeds rapidly to form acetylene and the corresponding organotin oxide. Diacetylene and monosubstituted diacetylenes react similarly (220). It is often advantageous to remove the water formed during the reaction by azeotropic techniques with benzene, toluene, or by other means (126, 210, 213). Triethyltin chloride, potassium hydroxide, and phenylacetylene when reacted at 100–110° for 2 hr are reported to yield triethyl(phenylethynyl)tin in 80% yield (216).

6. Miscellaneous Methods

(a) An interesting route to organotin acetylenes is the decarboxylation of triorganotin salts of acetylenemono- and dicarboxylic acids (104).

$$R_3SnOOCC{\equiv}CCOOSnR_3 \longrightarrow 2CO_2 + R_3SnC{\equiv}CSnR_3$$

(b) Alkynylsilicon and -germanium compounds also have been obtained from Wurtz–Fittig-type reactions of the corresponding organometallic halides with alkali-metals (33).

(c) Bis(trimethylsilyl)acetylene was formed from the interaction of tetrabromoethylene, magnesium, and trimethylchlorosilane in tetrahydrofuran in 60% yield (118).

(d) 1,2-Dichloroethane and tetrabromoethane are reported to react with phenyllithium and triphenylchlorosilane to produce triphenylchloroethynylsilane and triphenylbromoethynylsilane (46)

$$(C_6H_5)_3SiCl \xrightarrow[ClCH_2CH_2Cl]{C_6H_5Li} (C_6H_5)_3SiC{\equiv}CCl$$

$$(C_6H_5)_3SiCl \xrightarrow[Br_2CHCHBr_2]{C_6H_5Li} (C_6H_5)_3SiC{\equiv}CBr$$

(e) The tetralithium derivative of propyne has been reacted with trimethylchlorosilane (240).

(f) Tri-*n*-butylethynylgermane has been synthesized *via* dehydrohalogenation of tri-*n*-butylvinylgermane in a three-step reaction (114, 115)

$$(n\text{-}C_4H_9)_3GeCH{=}CH_2 + Br_2 \longrightarrow (n\text{-}C_4H_9)_3GeCHBrCH_2Br$$

$$(n\text{-}C_4H_9)_3GeCHBrCH_2Br + (C_2H_5)_2NH \xrightarrow{\text{xylene}} (n\text{-}C_4H_9)_3GeCBr{=}CH_2 + (C_2H_5)_2NH\cdot HBr$$

$$(n\text{-}C_4H_9)_3GeCBr{=}CH_2 + NaNH_2 \longrightarrow (n\text{-}C_4H_9)_3GeC{\equiv}CH + NaBr + NH_3$$

Some alkynylsilanes have also been synthesized through other dehalogenation-type reactions (1, 12).

B. ALKYNYLSILANES

The acetylenic silicon compounds (Tables XI–XIX) represent by far the largest group among the alkynyl compounds of the eleven elements reviewed in this paper. A recent book on organosilicon monomers reviews the synthesis and properties of alkynylsilanes up to the beginning of 1960 (136). The carbon–silicon bond in alkynylsilanes has considerable thermal and chemical stability. This allows alkynylsilanes to participate in many reactions without cleavage of the silicon–carbon bond and thus offers additional routes for the synthesis of new acetylenic silicon compounds.

TABLE XI

TETRAALKYNYLSILANES, $Si(C{\equiv}CR)_4$

Compound	Mp, °C	Yield, %	Method	Ref
$Si(C{\equiv}CH)_4$	88–89	...	1b	29
$Si(C{\equiv}CCl)_4$	117.5	73.5	1b	231
$Si(C{\equiv}CC_6H_5)_4$	197	...	..	94
$Si(C{\equiv}CC_6H_4Cl)_4$	215 dec	57	1b	67
$Si(C{\equiv}CC_6H_4Br)_4$	254 dec	52	1b	67
$Si(C{\equiv}CC_6H_{11})_4$	141	44.9	1b	66

1. *Reactions of Ethynylorganosilanes, $R_{4-n}Si(C{\equiv}CH)_n$*

A considerable number of ethynylsilanes are known, in particular of the type $R_3SiC{\equiv}CH$. Acetylenic Grignard compounds can be prepared in the well-known manner (10, 23, 98, 257)

$$R_3SiC{\equiv}CH + C_2H_5MgBr \longrightarrow R_3SiC{\equiv}CMgBr \quad (10)$$

The following reactions of trialkyl- and triarylsilylethynylmagnesium bromides are reported in the literature

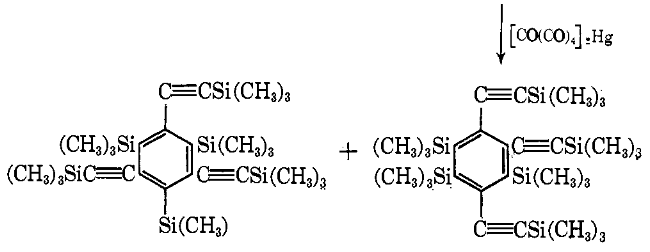
$$\begin{array}{lll}
R_3SiC{\equiv}CMgBr + & & \\
\quad X_2\,(X = Cl, Br, I) & \longrightarrow R_3SiC{\equiv}CX & (23, 160, 161) \\
\quad CO_2 & \longrightarrow R_3SiC{\equiv}CCOOH & (10, 161) \\
\quad (CH_3)_2C{=}O & \longrightarrow R_3SiC{\equiv}CC(OH)(CH_3)_2 & (10) \\
\quad CH_2{=}CHC(O)H & \longrightarrow R_3SiC{\equiv}CC(CH_3)(OH)CH_2Cl & (161) \\
\quad CH_3COCH_2Cl & \longrightarrow R_3SiC{\equiv}CCH(OH)CH{=}CH_2 & (161) \\
\quad ClC(O)OC_2H_5 & \longrightarrow R_3SiC{\equiv}CC(O)OC_2H_5 & (10) \\
\quad CH_2{=}CHCH_2Br & \longrightarrow R_3SiC{\equiv}CCH_2CH{=}CH_2 & (161) \\
\quad (CH_3)_3SiCl & \longrightarrow R_3SiC{\equiv}CSi(CH_3)_3 & (161)
\end{array}$$

$$(CH_3)_3SiC{\equiv}CC{\equiv}CC_2H_5 + RLi \longrightarrow (CH_3)_3SiC{\equiv}CCH{=}C(C_2H_5)R$$

The properties of vinylalkynylsilanes have already been reviewed (136). A detailed study of the bromination of such enyne systems has been published (224).

Recently several interesting acetylenic silicon derivatives have been prepared by the aromatization of diacetylenic derivatives using a mercuric cobalt tetracarbonyl reagent (69). The diacetylenic silicon starting material was synthesized from both an acetylenic Grignard or an acetylenic halide

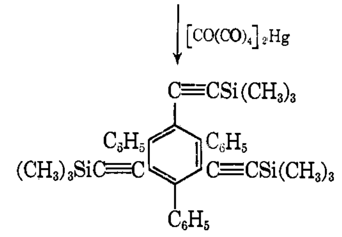
(a) $(CH_3)_3SiC{\equiv}CMgBr + CuCl_2 \longrightarrow (CH_3)_3SiC{\equiv}CC{\equiv}CSi(CH_3)_3$



mp 89–90° solidified and remelted 118–120°, 20% yield

mp 126–129°, 25% yield

(b) $(CH_3)_3SiC{\equiv}CBr + C_6H_5C{\equiv}CH \longrightarrow C_6H_5C{\equiv}CC{\equiv}CSi(CH_3)_3$



mp 213–214°

The yields vary between 40 and 80%. The sodium derivative of trimethylethynylsilane has also been prepared in liquid ammonia (10, 23). It was used in a similar manner as the Grignard reagents, but gave much lower yields. Trialkylethynylsilane also has been reported to undergo a Mannich-type reaction (10)

$$R_3SiC{\equiv}CH + CH_2O + HNEt_2 \longrightarrow R_3SiC{\equiv}CCH_2NEt_2 + H_2O$$

TABLE XII

TRIALKYNYLORGANOSILANES, $RSi(C\equiv CR')_3$

Compound	Mp, °C	Bp, °C (mm)	Yield, %	Method	Ref
$C_2H_5OSi(C\equiv CH)_3$		39–41 (1)	...	1b	19
$HSi[C\equiv CC(CH_3)_2OH]_3$	163–163.5		53	2	165, 192, 171
$CH_3Si[C\equiv CC(CH_3)_2OH]_3$	214		...	2	165, 171
$CH_2{=}CHSi[C\equiv CC(CH_3)_2OH]_3$	172.5–173		...	2	165, 192, 171
$CH_3Si(C\equiv CC_6H_5)_3$	126		70.5	1b	**64**

TABLE XIII

DIALKYNYLDIORGANOSILANES, $R_2Si(C\equiv CR')_2$

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(CH_3)_2Si(C\equiv CH)_2$	...	<50 (65)	...	...	1b	...	10, 29, 24
$(C_2H_5)_2Si(C\equiv CH)_2$	...	78–79 (84)	1.4393	0.8147	2	...	161
$(C_3H_7)_2Si(C\equiv CH)_2$	...	77.5–78.5 (15)	1.4429	0.8094	2	...	161
$(C_6H_5)_2Si(C\equiv CH)_2$	43, 44–45	...	...	...	2	...	29, 90
$(C_2H_5O)_2Si(C\equiv CH)_2$	...	31–32 (1)	...	...	1b	...	19
$(CH_3)_2Si(C\equiv CC_4H_9)_2$	...	68 (0.15)	1.4586	0.839	2	60	71
$(CH_3)_2Si(C\equiv CC_6H_5)_2$	80.5–81.5	...	...	...	2	64	71, 89
	76–78				1b		
$(C_2H_5O)_2Si(C\equiv CC_6H_5)_2$	...	185 (12)	1.5290[a]	1.0001[a]	1b	...	235
$(Et_3SiCH_2CH_2)(CH_3)Si(C\equiv CH)_2$	...	70–71 (1)	1.4630	0.8424	2	...	98
$(Et_2MeSiCH_2CH_2)(CH_3)Si(C\equiv CH)_2$	...	73–75 (1)	1.4580	0.8328	2	...	98
$(CH_3)_2Si[C\equiv CC(CH_3)_2OH]_2$	80–82	...	...	...	2	64	10, 163, 191
	107–108				1b		
$(CH_3)_2Si[C\equiv CC(CH_3)_2OAc]_2$	...	104 (3)	1.4639	0.9675	2	61	191
$(CH_3)_2Si[C\equiv CC(C_2H_5)_2OH]_2$	...	128–130 (0.5)	1.4629	0.9254	2	45	175
$(CH_3)_2Si[C\equiv CC(C_2H_5)_2OAc]_2$	...	148–149 (2)	1.4625	0.9650	2	30	175
$(CH_3)_2Si[C\equiv CC(CH_3)(C_2H_5)OH]_2$	85.5–87	...	...	...	2	55.5	173
$(CH_3)_2Si[C\equiv CC(CH_3)(C_2H_5)OAc]_2$	...	140–145 (4)	1.4707	0.9690	2	...	173
$(CH_3)_2Si[C\equiv CC(CH_3)(C_4H_9)OH]_2$	...	147 (4)	1.4670	0.9303	2	...	173
$(CH_3)_2Si[C\equiv CC(CH_3)(C_4H_9)OAc]_2$	...	174–176 (3)	1.4590	0.9641	2	...	173
$(CH_3)_2Si[C\equiv CC(OH)(Me)CH_2CHMe_2]_2$	...	141–143 (4)	1.4668	0.9226	2	...	173
$(CH_3)_2Si[C\equiv CC(OAc)(Me)CH_2CHMe_2]_2$	...	169–171 (4)	1.4600	0.9625	2	...	173
$(CH_3)_2Si[C\equiv CC(OH)(CH_3)C(CH_3)_3]_2$	64–65	...	...	...	2	...	175
$(CH_3)_2Si[C\equiv CC(Cl)(Me)Et][C\equiv CC(OH)(Me)Et]$	...	101–102 (0.7)	1.4863	0.9649	2	26	184
$(CH_3)_2Si[C\equiv CC(Me)Et_2][C\equiv CC(OH)(Me)Et]$	...	93–94 (3)	1.4901	0.9252	2	35	184
$(C_2H_5)_2Si[C\equiv CC(CH_3)_2OH]_2$	76–78	...	...	...	2	55	163, 191
$(C_2H_5)_2Si[C\equiv CC(CH_3)(C_4H_9)OH]_2$	70–71	...	...	...	2	...	173
$(C_2H_5)_2Si[C\equiv CC(CH_3)(C_4H_9)OAc]_2$	...	190 (2)	1.4586	0.9632	2	...	173
$(C_3H_7)_2Si[C\equiv CC(CH_3)_2OH]_2$	70–71	...	...	...	2	48	163, 191
$(C_6H_5)_2Si[C\equiv CC(CH_3)_2OH]_2$	123–124	...	...	...	2	...	164
$H(C_2H_5)Si[C\equiv CC(CH_3)_2OH]_2$	62–63	...	...	...	2	...	164
$(CH_3)(C_2H_5)Si[C\equiv CC(CH_3)_2OH]_2$	80.5–81.5	...	...	...	2	...	164, 166
$(CH_3)(C_3H_7)Si[C\equiv CC(CH_3)_2OH]_2$	78–79	...	...	...	2	...	164, 166
$(CH_3)(C_6H_5)Si[C\equiv CC(CH_3)_2OH]_2$	129–130	...	...	...	2	47	164
$(CH_3)(C_6H_5)Si[C\equiv CC(CH_3)_2OAc]_2$	...	178–179 (4)	1.5112	1.0281	2	...	164
$(CH_3)(C_{10}H_7)Si[C\equiv CC(CH_3)_2OH]_2$	92–93	...	...	...	2	...	164
$(CH_3)(C_2H_5)Si[C\equiv CC(CH_3)(C_2H_5)OH]_2$	60	...	...	...	2	...	173
$(CH_3)(C_3H_7)Si[C\equiv CC(CH_3)(C_2H_5)OH]_2$	50–51	...	...	...	2	...	173
$(CH_3)(C_3H_7)Si[C\equiv CC(CH_3)(C_2H_5)OAc]_2$	...	156–158 (4)	1.4655	0.9450	2	...	173
$(C_2H_5)(C_6H_5)Si[C\equiv CC(CH_3)_2OH]_2$	92–93	...	...	...	2	...	164
$Cl(CH_3)Si[C\equiv CC_4H_9\text{-}n]_2$	...	148–150 (8)	...	...	2	...	39
$(MeEt_2SiCH_2CH_2)(Me)Si[C\equiv CC(CH_3)_2OH]_2$	...	105 (2)	1.4720	...	2	...	98
$(Et_3SiCH_2CH_2)(Me)Si[C\equiv CC(CH_3)_2OH]_2$	44.8–46.3	158 (2)	...	...	2	64	96, 98
		154–156 (1)	1.4730				
$(CH_3)_2Si[C\equiv CCH{=}CH_2]_2$	...	67–68 (9)	1.5108	0.8495	2	...	138, 140
$(CH_3)_2Si[C\equiv CC(CH_3){=}CH_2]_2$	...	75 (4)	1.5000	0.8475	[b]	...	170
$(C_2H_5)_2Si[C\equiv CCH{=}CH_2]_2$	...	84–86 (8)	1.5140	0.8556	2	...	138, 140
$(C_2H_5)_2Si[C\equiv CC(CH_3){=}CH_2]_2$	...	105 (6)	1.5027	0.8594	[b]	...	170
$(C_3H_7)_2Si[C\equiv CCH{=}CH_2]_2$	...	82–86 (5)	1.5145	0.8561	2	...	138, 140
$(Cl)(H)Si[C\equiv CCH{=}CH_2]_2$	...	88–89 (12)	1.5224	0.9471	2	...	140
$(CH_3)(H)Si[C\equiv CCH{=}CH_2]_2$	...	60.5–61 (8)	1.5182	0.8581	[b]	...	136
$(C_2H_5)(H)Si[C\equiv CC(CH_3){=}CH_2]_2$	...	76 (4)	1.5010	0.8518	[b]	...	167, 170
$(CH_3)(C_2H_5)Si[C\equiv CC(CH_3){=}CH_2]_2$	...	87 (2)	1.5000	0.8583	[b]	...	170
$(CH_3)(C_3H_7)Si[C\equiv CC(CH_3){=}CH_2]_2$	...	113 (10)	1.4990	0.8550	[b]	...	170

[a] 9°. [b] Synthesized from other acetylenic compounds.

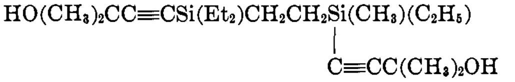
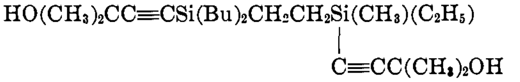
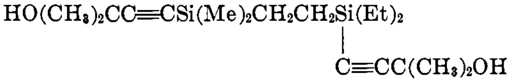
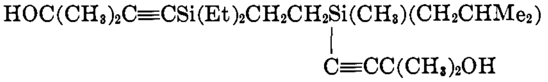
TABLE XIV
MONOALKYNYLSILANES, $R_3SiC\equiv CR$

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$H_3SiC\equiv CH$	−90.7	−22.4	. . .	. . .	2	. . .	34
$(CH_3)_3SiC\equiv CH$	. . .	51–52, 53.5	1.3870[a]	0.707[b]	1b, 2	52	10, 22, 101, 221, 239
$(C_2H_5)_3SiC\equiv CH$	. . .	138 (771)	1.4302	0.7862	2	. . .	139, 160
$(C_3H_7)_3SiC\equiv CH$	. . .	97–97.5 (20)	1.4376	0.7980	2	. . .	161
$(C_6H_5)_3SiC\equiv CH$	48.5–49	146–149 (0.03)	1.6180	. . .	1b	. . .	10, 46, 161, 239
	45–46	191 (1.9)					
$(C_2H_5O)_3SiC\equiv CH$	. . .	91–91.5 (52)	1.3982	. . .	1b	. . .	19
$(CH_3)_2(C_2H_5)SiC\equiv CH$	. . .	83.2 (751)	1.4082	0.7435		74.7	121, 221
$(C_2H_5)_2(CH_3)SiC\equiv CH$	. . .	112–113	1.4200	0.7635	2	60.5	129
$(CH_3)_2(OH)SiC\equiv CH$	. . .	47–48 (46)	1.4168	0.8858	2	50	88, 201
		46 (20)	1.4138	0.8898			
$H(CH_2{=}CH)_2SiC\equiv CH$	. . .	−40	. . .	. . .	. . .	. . .	244
$H(CH_3)(C_6H_5)SiC\equiv CH$	. . .	92.5 (42)	1.5159	0.9169	2	. . .	161
$H(C_2H_5)(C_6H_5)SiC\equiv CH$	. . .	90 (17)	1.5161	0.9161	2	. . .	161
$Cl_3SiC\equiv CBr$	. . .	76–80 (11)	1.5240[a]	. . .	6f	. . .	1
$Cl_3SiC\equiv CC_6H_5$	. . .	132–135 (26)	1.5527	1.2871	2	. . .	2, 122, 136, 142
$Cl_2(CH_3)SiC\equiv CC_3H_7$	. . .	168–169	. . .	. . .	2	52.5	39
$Cl_2(CH_3)SiC\equiv CC_4H_9$	. . .	187–188	. . .	. . .	2	55.5	39
$(CH_3)_3SiC\equiv CBr$	. . .	48 (50)	1.4612	. . .	*c*	. . .	23
$(CH_3)_3SiC\equiv CI$	. . .	53 (15)	1.5109	. . .	*c*	. . .	23
$(CH_3)_3SiC\equiv CCH_3$	. . .	99–100 (760)	1.4091	0.7581	2	. . .	139
$(CH_3)_3SiC\equiv CCH_2Cl$	. . .	50 (17)	1.4546	0.9295	*c*	92.5	85
$(CH_3)_3SiC\equiv CCH_2N(C_2H_5)_2$	. . .	92–95 (34)	. . .	. . .	1b	. . .	10
$(CH_3)_3SiC\equiv CCH(CH_3)Cl$	. . .	45–46 (10)	1.4512	0.9084	2	68.3	200
$(CH_3)_3SiC\equiv CCH(C_2H_5)Cl$	. . .	46–47 (5)	1.4540	0.9090	2	60	194
$(CH_3)_3SiC\equiv CC(CH_3)_2Cl$	. . .	32–35 (5)	1.4503	0.9043	*c*	87	177, 198
		49 (14)	1.4415	0.8774			
$(CH_3)_3SiC\equiv CC(CH_3)(C_2H_5)Cl$	. . .	38–40 (2)	1.4502	0.9015	*c*	54	177, 198
		61–62 (8)	1.4602	0.9082			
$(CH_3)_3SiC\equiv CC(CH_3)(Cl)C(CH_3)_3$	41	54–55 (2)	. . .	. . .	*c*	. . .	177
$(CH_3)_3SiC\equiv CCH(Br)CH(CH_3)Br$	. . .	85–86.5 (3)	1.5342	1.3930	2	. . .	224
$(CH_3)_3SiC\equiv CC(CH_3)(Br)CH_2Br$	. . .	84–85 (5)	1.5125	1.3820	2	. . .	224
$(CH_3)_3SiC\equiv CC_3H_7$	. . .	133–134	1.4272[a]	0.765[a]	2	52	39, 41
$(CH_3)_3SiC\equiv CC_4H_9$	. . .	155	1.4318[a]	0.768[a]	2	46	39, 41, 140
$(CH_3)_3SiC\equiv CC_5H_9$[d]	. . .	89–89.5 (20)	1.4928	0.8551	2	. . .	225
$(CH_3)_3SiC\equiv CC_6H_{11}$[e]	. . .	107–108 (20)	1.4940	0.8616	2	40	224
$(CH_3)_3SiC\equiv CC_6H_5$	. . .	214 (760)	1.5262[a]	. . .	1b, 2	80	33, 139, 145, 248
		87.5 (9)	1.5284	0.8961			
$(CH_3)_3SiC\equiv CC_6H_4Br\text{-}m$	. . .	96 (1.9)	1.5532[a]	. . .	1b, 2	90	33
$(CH_3)_3SiC\equiv CC_6H_4CH_3\text{-}p$	. . .	115 (15.5)	1.5328[a]	. . .	1b, 2	85	33
$(CH_3)_3SiC\equiv CC_6H_4CH_3\text{-}o$	. . .	74 (2.2)	1.5218[a]	. . .	1b, 2	74	33
$(CH_3)_3SiC\equiv CC_6H_4OCH_3\text{-}p$	. . .	96 (1.5)	1.5448[a]	. . .	1b, 2	68	33
$(CH_3)_3SiC\equiv CCH[C(C_6H_5)_3]CH_2C(C_6H_5)_3$	178	. . .	. . .	. . .	*c*	62	131
$(CH_3)_3SiC\equiv CCOOH$	. . .	95–97 (7–8)	1.4490[a]	. . .	1b	. . .	10
$(CH_3)_3SiC\equiv CCOOC_2H_5$	. . .	92.5–96 (25)	. . .	. . .	1b	. . .	10
$(CH_3)_3SiC\equiv CC(CH_3)_2OOC(CH_2)_4COOH$	. . .	178–180 (4)	1.4548	0.9902	*c*	36	196
$(CH_3)_3SiC\equiv CCH_2CH(COCH)_3COOC_2H_5$	. . .	110–111 (10)	1.4511	0.9583	*c*	40	193
$(CH_3)_3SiC\equiv CCH(CH_3)CH(COCH_3)COOC_2H_5$	. . .	52–53 (15)	1.4368	0.9204	2	34.6	200
$(CH_3)_3SiC\equiv CCH(SiMe_3)_2$	. . .	80–85 (19)	. . .	. . .	6e	50	240
$(CH_3)_3SiC\equiv CCH_2CH_2CH{=}CH_2$	. . .	44 (10)	1.4420	0.7888	*c*	. . .	38
$(CH_3)_3SiC\equiv CCH_2CH_2CH{=}CHC_2H_5$	. . .	. . .	. . .	. . .	*c*	. . .	38
$(CH_3)_3SiC\equiv COC_2H_5$	. . .	57.2 (34)	1.424	0.8276	2	. . .	162
$(CH_3)_3SiC\equiv COC_4H_9\text{-}n$	. . .	83–84 (32)	1.4305	0.8268	2	. . .	162
$(C_2H_5)_3SiC\equiv CCH_3$	. . .	169.5–170.5	1.4485	0.8029	2	. . .	139
$(C_2H_5)_3SiC\equiv CCH_2Cl$	. . .	72 (6)	1.4698	0.9262	*c*	95	85
$(C_2H_5)_3SiC\equiv CCH(CH_3)Cl$	. . .	64–65 (2)	1.4642	0.9043	2	64.6	200
$(C_2H_5)_3SiC\equiv CCH(C_2H_5)Cl$	. . .	96.5–98.5 (8)	1.4641	0.9048	*c*	60.5	194
$(C_2H_5)_3SiC\equiv CC(CH_3)_2Cl$	. . .	101–102 (16)	1.4525	0.8861	*c*	50	198
$(C_2H_5)_3SiC\equiv CC(CH_3)_2CH_2Cl$	. . .	122 (5)	1.4725	0.9663	2	. . .	160
$(C_2H_5)_3SiC\equiv C\underline{C(CH_3)CH_2O}$	. . .	99.5 (6)	1.4580	0.8775	2	. . .	160
$(C_2H_5)_3SiC\equiv CCH_2(CH_2)_4CH_3$	. . .	93.5–94 (3)	1.4560	0.8118	2	. . .	140

TABLE XIV (*Continued*)

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(C_2H_5)_3SiC{\equiv}CCH(C_2H_5)(CH_2)_4CH_3$	...	98–99 (3)	1.4520	0.8069	2	...	140
$(C_2H_5)_3SiC{\equiv}CCH[Si(CH_3)_3](CH_2)_4CH_3$	...	108–109 (3)	1.4555	0.8180	2	...	140
$(C_2H_5)_3SiC{\equiv}CC_6H_5$	...	133–133.5 (10)	1.5259	0.8984	2	...	139
$(C_2H_5)_3SiC{\equiv}COC_2H_5$	...	73 (34)	1.4448	0.8603	2	...	162
$(C_2H_5)_3SiC{\equiv}CCH_2OCH_2OC_4H_9$	...	122–123 (1)	1.4492	0.8834	*c*	...	188
$CH_3(C_2H_5)_2SiC{\equiv}CCH_2OCH_2OC_4H_9$	...	90–91 (0.2)	1.4432	0.8850	*c*	...	188
$C_2H_5(CH_3)_2SiC{\equiv}CC(CH_3)_2OCH_2OC_4H_9$	...	103–104 (1)	1.4415	0.8650	*c*	...	188
$C_2H_5(CH_3)_2SiC{\equiv}CCH(C_3H_7)OCH_2OC_4H_9$	...	116–117 (1)	1.4665	0.8520	*c*	...	188
$C_3H_7(C_2H_5)_2SiC{\equiv}CC(CH_3)(C_2H_5)OCH_2OC_4H_9$	...	105–107 (0.5)	1.4370	0.8512	*c*	...	188
$C_2H_5(CH_3)_2SiC{\equiv}CC(CH_3)(C_2H_5)OCH_2OC_4H_9$	...	106–108 (0.5)	1.4420	0.8660	*c*	...	188
$(C_2H_5)_3SiC{\equiv}CC(CH_3)(C_2H_5)OCH_2OC_4H_9$	...	113–114 (0.6)	1.4410	0.8636	*c*	...	188
$(C_2H_5)SiC{\equiv}CC(CH_3)_2OCH_2OC_4H_9$	...	108–110 (0.6)	1.4459	0.8671	*c*	...	188
$(C_2H_5)_3SiC{\equiv}CC(CH_3)_2OCH_2OC_3H_7$	...	98–100 (0.5)	1.4409	0.8685	*c*	...	188
$(C_2H_5)SiC{\equiv}CC(CH_3)_2OCH_2OC_3H_7\text{-}i$	...	90–93 (0.5)	1.4321	0.8715	*c*	...	188
$(C_2H_5)_3SiC{\equiv}CCH(C_3H_7)OCH_2OC_4H_9$	...	104–105 (2)	1.4530	0.8742	*c*	...	188
$(C_2H_5)_3SiC{\equiv}CCH(C_3H_7)OCH_2OC_4H_9$	...	104–105 (2)	1.4530	0.8742	*c*	...	188
$(C_2H_5)_3SiC{\equiv}CCOOH$	...	132.2 (3)	1.4682	0.9639	*c*	...	160
$(C_2H_5)_3SiC{\equiv}CCH_2CH_2COOH$	...	78–80 (10)	1.4520	0.9478	*c*	19	193
$(C_2H_5)_3SiC{\equiv}CCH_2CH_2COOR^f$	...	94–95 (8)	1.4572	0.9311	*c*	80	193
$(C_2H_5)_3SiC{\equiv}CCH_2CH(COCH_3)(COOH)$	...	70–78 (3)	1.4410	0.9408	*c*	53	193
$(C_2H_5)_3SiC{\equiv}CCH_2CH(COCH_3)COOC_2H_5$	...	155–157 (10)	1.4585	0.9448	*c*	45	193
$(C_2H_5)_3SiC{\equiv}CCH(CH_3)CH(COCH_3)COOH$	...	68–69 (2)	1.48	0.9587	*c*	50.5	200
$(C_2H_5)_3SiC{\equiv}CCH(CH_3)CH(COCH_3)COOC_2H_5$	...	60 (1)	1.4600	0.9222	*c*	32.1	200
$(C_2H_5)_3SiC{\equiv}CCH(CH_3)OCH_2CH_2COC_2H_5$	...	96 (6)	1.4600	0.8946	*c*	38.8	200
$(C_2H_5)_3SiC{\equiv}CC(CH_3)_2OOC(CH_2)_4COOH$	...	63–65 (14)	1.4610	0.8135	*c*	32	196
$(C_2H_5O)_3SiC{\equiv}CC_6H_5$	...	141–142 (2)	1.4898^g	0.986^g	2	...	235
$(C_6H_5)_3SiC{\equiv}CCl$	101–102	...	...	...	6d	...	46
$(C_6H_5)_3SiC{\equiv}CBr$	111–113	...	...	...	6d	...	46
$(C_6H_5)_3SiC{\equiv}CCH_3$	113–114	...	...	...	1b, 2	...	2, 10, 136, 139
$(C_6H_5)_3SiC{\equiv}CC_6H_5$	100–101	...	...	...	1b	72	43–45
$(CH_3)_2(C_2H_5)SiC{\equiv}CCH(CH_3)Cl$	...	70 (13)	1.4608	0.9057	*c*	81.8	87
$(CH_3)_2(C_3H_7)SiC{\equiv}CC(CH_3)_2Cl$	...	70–71 (9)	1.4454	0.8748	*c*	...	181
$(CH_3)_2(C_4H_9)SiC{\equiv}CC(CH_3)_2Cl$	...	80–81 (8)	1.4476	0.8753	*c*	...	181
$(CH_3)_2(C_6H_5)SiC{\equiv}CCH_2Cl$	...	118 (6)	1.5345	1.0409	*c*	90.5	85
$(CH_3)_2(C_6H_5)SiC{\equiv}CCH_2CH(COCH_3)COOC_2H_5$	...	149–151 (6)	1.5095	1.0140	*c*	51	193
$(CH_3)(CH_3COO)_2SiC{\equiv}CC_3H_7$	...	96–102 (0.3)	...	...	2	85	39
$(CH_3)(CH_3COO)_2SiC{\equiv}CC_4H_9$	...	102–106 (0.3)	...	...	2	83	39
$(CH_3)(C_2H_5)_2SiC{\equiv}CC(CH_3)_2Cl$	...	49–50 (0.2)	1.4490	0.8984	*c*	...	181
$(C_2H_5O)_3SiC{\equiv}CC_6H_5$	...	141–142 (6)	1.4898^g	0.986^g	2	...	235
$(CH_3)_3SiC{\equiv}CCH(CH_3)SH$	...	54–55 (8)	1.4664	0.8650	*c*	65	87
$(CH_3)_3SiC{\equiv}CCH(CH_3)(SHgCl)$	132	...	...	...	*c*	...	87
$(CH_3)_3SiC{\equiv}CCH(CH_3)SCN$	...	80 (2.5)	1.4830	0.9285	*c*	35	87
$(CH_3)_3SiC{\equiv}CCH(CH_3)SR^f$	...	107–108 (2)	1.4665	0.8798	*c*	42.3	87
$(CH_3)_3SiC{\equiv}CCH(CH_3)SCH_2CH_2OC_4H_9$	...	62 (5)	1.4418	0.8431	*c*	47	87
$(CH_3)_2(C_2H_5)SiC{\equiv}CCH(CH_3)SH$	...	74 (10)	1.4745	0.8700	*c*	58	87
$(CH_3)_2(C_2H_5)SiC{\equiv}CCH(CH_3)SHgCl$	145	...	...	...	*c*	...	87
$(CH_3)_2(C_2H_5)SiC{\equiv}CCH(CH_3)SCN$	...	90 (2)	1.4889	0.9357	*c*	...	87
$(CH_3)_2(C_2H_5)SiC{\equiv}CCH(CH_3)SR^f$	...	60 (1)	1.4529	0.8650	*c*	45	87
$(CH_3)_2(C_2H_5)SiC{\equiv}CCH(CH_3)SCH_2CH_2OC_4H_9$	...	121 (2.5)	1.4700	0.8839	*c*	42	87
$(CH_3)_3SiC{\equiv}CCHO^h$	195	...	...	...	*c*	...	207
$(CH_3)_2(C_2H_5)SiC{\equiv}CCHO^h$	172	...	...	...	*c*	...	207
$(CH_3)_2(C_2H_5)SiC{\equiv}CAc^h$	84	...	...	...	*c*	...	207
$(CH_3)_2(C_2H_5)SiC{\equiv}CCOC_2H_5{}^h$	86	...	...	...	*c*	...	207
$(CH_3)_3SiC{\equiv}CAc^h$	99	...	...	...	*c*	...	207
$(CH_3)_3SiC{\equiv}CBz^h$	190	...	...	...	*c*	...	207
$(CH_3)_3SiC{\equiv}CCOCH{=}CH_2{}^h$	101	...	...	...	*c*	...	207
$(CH_3)_3SiC{\equiv}CCOC{\equiv}CCH{=}CH_2{}^h$	85	...	...	...	*c*	...	207
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2Cl$	...	78–79 (3)	1.4605	0.9044	*c*	61.3	199
$(CH_3)_3SiC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)_2Cl$	...	93–94 (6)	1.4666	0.8982	*c*	52.2	199
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3){=}CH_2$	...	90–91 (7)	1.4658	0.8187	2	63.7	199
$(CH_3)_3SiC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}C(CH_3){=}CH_2$	...	89–90 (6)	1.4732	0.8745	2	64	199
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_3$	...	53–54 (4)	1.4526	0.8245	*c*	...	177
$(CH_3)_3SiC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)_3$	...	56–58 (2)	1.4368	0.8035	*c*	...	177

TABLE XIV (*Continued*)

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(CH_3)_3SiC{\equiv}CC(CH_3)(CMe_3)C{\equiv}CC(CH_3)_3$	55	70–72 (4)	...	...	*c*	...	177
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CCH_2OH$	...	98–99 (2)	1.4736	0.8973	2	41.2	199
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CCH_2OR^f$	...	133–134 (5)	1.4590	0.8993	*c*	66.0	199
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CCH(CH_3)OH$	...	116 (12)	1.4675	0.8930	2	27.4	199
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CCH(CH_3)OR^f$	...	121–122 (2)	1.4465	0.8670	*c*	65.7	199
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OH$	41–42	102 (7)	...	...	2	64.8	199
$(CH_3)_3SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OR^f$	...	134–135 (9)	1.4439	0.8523	*c*	65.6	199
$(CH_3)_3SiC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)_2OH$	...	105 (6)	1.4697	0.8867	2	25	199
$(CH_3)_3SiC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)_2OR^f$	...	122–123	1.4502	0.8786	*c*	61.2	199
$CH_3(C_2H_5)_2SiC{\equiv}CC(CH_3)_2C{\equiv}CCH(C_3H_7)OH$	...	90–92 (3)	1.4995	0.8990	*c*	...	181
$CH_3(C_2H_5)_2SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OH$	...	78–80 (0.2)	1.4683	0.8800	*c*	...	181
$(CH_3)_2(C_3H_7)SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OH$	...	103–104 (5)	1.4463	0.8531	*c*	...	181
$(CH_3)_2(C_4H_9)SiC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OH$	...	104–105 (4)	1.4458	0.8519	*c*	...	181
 $HO(CH_3)_2CC{\equiv}CSi(Et_2)CH_2CH_2\underset{C{\equiv}CC(CH_3)_2OH}{Si}(CH_3)(C_2H_5)$	44–45	167–169 (5) 163–164 (1)	... 1.4802	... 0.9185	2	34 45	96, 98
 $HO(CH_3)_2CC{\equiv}CSi(Bu)_2CH_2CH_2\underset{C{\equiv}CC(CH_3)_2OH}{Si}(CH_3)(C_2H_5)$	...	163–165 (4)	1.4802	0.8980	2	20	96
 $HO(CH_3)_2CC{\equiv}CSi(Me)_2CH_2CH_2\underset{C{\equiv}CC(CH_3)_2OH}{Si}(Et)_2$	35.5– 36.5	140 (1)	...	...	2	70	96
$(CH_3)_3SiC{\equiv}CC({=}CH_2)C{\equiv}C(OH)C{\equiv}CSi(CH_3)_3$	...	136 (1)	...	...	*c*	...	15
 $HOC(CH_3)_2C{\equiv}CSi(Et)_2CH_2CH_2\underset{C{\equiv}CC(CH_3)_2OH}{Si}(CH_3)(CH_2CHMe_2)$	...	162–164 (3)	1.4805	0.9086	2	45	98

[a] 25°. [b] 24°. [c] Synthesized from other acetylenic compounds. [d] Cyclopentyl. [e] Cyclohexyl. [f] Ethyl butyl ether (see footnote *a*, Table XV). [g] 21°. [h] Obtained as 3,5-dinitrobenzoyl hydrazide. Report of synthesis of parent compound could not be found in the literature.

2. *Reactions of Alkynylorganosilanes,* $R_{4-n}Si(C{\equiv}CR)_n$

Many reactions of alkynylsilanes have been studied and described (136). More recently one class of silanes, the silicon acetylenic alcohols $R_{4-n}Si(C{\equiv}CCR_2OH)_n$, has attracted increasing attention. The tertiary alcohols so formed react with gaseous hydrogen chloride or concentrated hydrochloric acid to form the corresponding chlorides in good yields (177, 198)

$$R_3SiC{\equiv}CR_2OH + HCl \longrightarrow R_3SiC{\equiv}CCR_2Cl + H_2O$$

Thionyl chloride has been reacted with primary, secondary, and tertiary alcohols (85, 87, 194, 198, 200)

$$R_3SiC{\equiv}CCR_2OH + SOCl_2 \longrightarrow R_3SiC{\equiv}CR_2Cl + SO_2 + HCl$$

The same alcohols react with butyl vinyl ether to form acetal derivatives (175, 180, 200)

$$R_3SiC{\equiv}CCR_2OH + CH_2{=}CHOC_4H_9 \longrightarrow R_3SiC{\equiv}CCR_2OCH(CH_3)OC_4H_9$$

Cyanoethylation in the presence of sodium methoxide results in the formation of the cyanoethyl esters (196, 200)

$$R_3SiC{\equiv}CCR_2OH + CH_2{=}CHCN \longrightarrow R_3SiC{\equiv}CCR_2OCH_2CH_2CN$$

These ethers in turn form the corresponding ketones with ethylmagnesium bromide (196)

$$R_3SiC{\equiv}CCR_2OCH_2CH_2CN + C_2H_5MgBr \longrightarrow R_3SiC{\equiv}CCR_2OCH_2CH_2C(O)C_2H_5$$

Primary silicon acetylenic chlorides react easily with sodium acetoacetic ester yielding the corresponding keto esters (193).

$$R_3SiC{\equiv}CCH_2Cl + CH_3COCHNaCOOC_2H_5 \longrightarrow R_3SiC{\equiv}CCH_2CH(COCH_3)COOC_2H_5 + NaCl$$

From the reaction of the sodium malonic ester with the chloride the acid was obtained instead of the ester. It is assumed that the ester was cleaved during the reaction.

$$R_3SiC{\equiv}CCH_2Cl + NaCH(OOCC_2H_5)_2 \longrightarrow$$

$$[R_3SiC{\equiv}CCH_2CH(OOCC_2H_5)_2] + NaCl \xrightarrow{H_2O} R_3SiC{\equiv}CCH_2CH_2COOH + CO_2 + 2C_2H_5OH \quad (193)$$

The silicon acetylenic halides can also be utilized to synthesize silylacetylenic thiols

$$R_3SiC{\equiv}CCH(CH_3)Cl + NaSH \longrightarrow R_3SiC{\equiv}CCH(CH_3)SH + NaCl$$

$$R_3SiC{\equiv}CCH(CH_3)SCN + BrMgC_2H_5 \longrightarrow R_3SiC{\equiv}CCH(CH_3)SH \quad (87)$$

Primary and secondary alcohols undergo partial or complete esterification with adipic acid, depending on the reaction conditions (196).

$$R_3SiC{\equiv}CCH_2OH + HOOC(CH_2)_4COOH \longrightarrow R_3SiC{\equiv}CCH_2OOC(CH_2)_4COOH + H_2O$$

TABLE XV

SILICON ACETYLENIC ALCOHOLS, $R_3SiC\equiv C(CR_2)_nOH$

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(CH_3)_3SiC\equiv CCH_2OH$	...	61 (2)	1.4523	0.8806	2	40.2	84
$(CH_3)_3SiC\equiv CCH_2OR^a$	...	95 (5)	1.4378	0.8683	*b*	71	84
$(CH_3)_3SiC\equiv CCH(CH_3)OH$	...	76 (15)	1.4442	0.8614	2	60	200
$(CH_3)_3SiC\equiv CCH(CH_3)OR^a$	...	98 (5)	1.4320	0.8540	*b*	51.5	200
$(CH_3)_3SiC\equiv CCH(CH_3)OCH_2CH_2CN$	...	90 (8)	1.4385	0.8689	*b*	44.0	200
$(CH_3)_3SiC\equiv CCH(C_2H_5)OH$	...	57.5 (3)	1.4452	0.8604	2	55	194
$(CH_3)_3SiC\equiv CCH(C_2H_5)OR^a$	...	102–103 (8)	1.4368	0.8580	*b*	41.6	194
$(CH_3)_3SiC\equiv CC(CH_3)_2OH$	41–41.8	80.5 (35)	...	...	*b*	...	10
	42–42.5	71 (18)	...	...	2	62	190
	...	94–96 (54)	...	...	2	...	196
$(CH_3)_3SiC\equiv CC(CH_3)_2OR^a$	...	85–86 (3)	1.4331	0.8541	*b*	66.4	190
$(CH_3)_3SiC\equiv CC(CH_3)_2OCH_2CH_2CN$	...	120 (14)	1.4452	0.8875	*b*	60	196, 197
$(CH_3)_3SiC\equiv CC(CH_3)_2OCH_2CH_2OC_2H_5$	...	133–134 (25)	1.4440	0.8798	*b*	22.1	196
$(CH_3)_3SiC\equiv CC(C_2H_5)_2OH$	...	69–70 (1.5)	1.4459	0.8435	2	40.13	175
$(CH_3)_3SiC\equiv CC(C_2H_5)_2OR^a$	...	95–96 (1)	1.4401	0.8625	*b*	33.11	175
$(CH_3)_3SiC\equiv CC(CH_3)(C_2H_5)OH$	...	123 (7)	1.4410	0.8484	2	30	172
$(CH_3)_3SiC\equiv CC(CH_3)(C_2H_5)OR^a$	...	145–146 (7)	1.4360	0.8643	*b*	...	172
$(CH_3)_3SiC\equiv CCH(C_3H_7)OH$	...	89 (4)	1.4374	0.8426	2	...	172
$(CH_3)_3SiC\equiv CCH(C_3H_7)OR^a$	...	...	1.4370	0.8598	*b*	...	172
$(CH_3)_3SiC\equiv CC(CH_3)(C_4H_9)OH$	...	82–85 (2)	1.446	0.8414	2	...	172
$(CH_3)_3SiC\equiv CC(CH_3)(C_4H_9)OR^a$	...	140 (4)	1.4421	0.8651	*b*	...	172
$(CH_3)_3SiC\equiv CC(CH_3)(CMe_3)OH$	...	62–63 (3)	1.4348	0.8171	2	...	172, 175
	32	64–65 (3)	...	...	...	...	...
$(CH_3)_3SiC\equiv CC(CH_3)(CMe_3)OR^a$	...	134–136 (4)	1.4332	0.8567	*b*	...	172, 175
	...	95–97 (2)	1.4404	0.8598	...	...	...
$(CH_3)_3SiC\equiv CC(CH_3)(CMe_3)OCH(OH)CCl_3$	...	92–94 (0.5)	1.4656	1.077	*b*	...	179
$(CH_3)_3SiC\equiv CCH_2CH_2OH$	...	70 (6)	1.4507	0.8742	2	38.5	217
$(CH_3)_3SiC\equiv CCH_2CH_2OR^a$	...	92 (4)	1.4383	0.8617	*b*	67.3	217
$(CH_3)_3SiC\equiv CCH_2CH(CH_3)OH$	...	95–97 (2)	1.4748	0.9101	...	16.4	85
		84 (2)	1.4661	0.8908	2	43.7	217
$(CH_3)_3SiC\equiv CCH_2CH(CH_3)OR^a$	...	153 (3)	1.4655	0.8925	...	97.5	85
	...	108 (3)	1.4451	0.8787	*b*	74	217
$(CH_3)_3SiC\equiv CC_6H_{10}OH$-*m*^{c}	71.5–72.5	127 (24)	...	...	2	...	144
$(CH_3)_3SiC\equiv CCH(OH)C_4H_3O^d$	...	92 (3)	1.4908	0.9949	2	53	212
$(C_2H_5)_3SiC\equiv CCH_2OH$	...	100–102 (4)	1.4633	0.8923	2	...	84
		109–110 (6)	1.4670	0.8932	...	44.7	189
$(C_2H_5)_3SiC\equiv CCH_2OR^a$	...	91–94 (1)	1.4492	0.8834	*b*	...	189
$(C_2H_5)_3SiC\equiv CCH(CH_3)OH$	...	120 (25)	1.4605	0.8697	2	56.5	200
$(C_2H_5)_3SiC\equiv CCH(CH_3)OR^a$	...	110–111 (2)	1.4462	0.8715	*b*	48.3	200
$(C_2H_5)_3SiC\equiv CCH(CH_3)OCH_2CH_2CN$	...	124 (1)	1.4590	0.9062	*b*	69.1	200
$(C_2H_5)_3SiC\equiv CCH(C_2H_5)OH$	...	106 (7)	1.4601	0.8851	2	44.6	194
$(C_2H_5)_3SiC\equiv CCH(C_2H_5)OR^a$	...	138–139 (2.5)	1.4500	0.8736	*b*	48	194
$(C_2H_5)_3SiC\equiv CCH(C_3H_7)OH$	...	97–98 (2)	1.4600	0.8708	2	...	180
$(C_2H_5)_3SiC\equiv CCH(C_3H_7)OR^a$	...	151–153 (12)	1.4545	0.8801	*b*	...	180
$(C_2H_5)_3SiC\equiv CC(CH_3)_2OH$	...	121.8 (27)	1.4557	0.8638	2	71.2	139, 190
$(C_2H_5)_3SiC\equiv CC(CH_3)_2OCH_2CH_2CN$	...	140–140.5 (4)	1.4513	0.8925	*b*	50	196, 197
$(C_2H_5)_3SiC\equiv CC(CH_3)(C_2H_5)OH$	...	98–102 (2)	1.4425	0.8617	2	...	172
$(C_2H_5)_3SiC\equiv CC(CH_3)(C_2H_5)OR^a$	...	135–136 (2)	1.4275	0.8618	*b*	...	172, 186
$(C_2H_5)_3SiC\equiv CC(CH_3)(C_4H_9)OH$	...	99–102 (2)	1.4456	0.8505	2	...	172
$(C_2H_5)_3SiC\equiv CC(CH_3)(C_4H_9)OR^a$	...	136–138 (2)	1.4441	0.8620	*b*	...	172
$(C_2H_5)_3SiC\equiv CC_6H_{10}OH$-*o*^{e}	...	161 (22)	1.4822	0.9195	2	43	144
$(C_6H_5)_3SiC\equiv CC(CH_3)_2OH$	118	236 (5)	...	...	2	...	144
$(CH_3)_2(CH_2Cl)SiC\equiv CC(CH_3)_2OH$	...	82–85 (5)	1.4696	0.999	2	22.5	183
$(CH_3)_2(CH_2Cl)SiC\equiv CC(CH_3)_2OR^a$	...	108–109 (6)	1.4564	0.9592	*b*	...	183
$(CH_3)_2(CH_2Cl)SiC\equiv CC(CH_3)(C_2H_5)OH$	...	97–98 (5)	1.4674	0.9865	2	...	183
$(CH_3)_2(C_2H_5)SiC\equiv CCH_2OH$	...	78–80 (8)	1.4462	0.8740	2	...	84, 189
	...	131–132 (2)	1.5335	0.9996		67.8	...
$(CH_3)_2(C_2H_5)SiC\equiv CCH(CH_3)OH$	...	92 (14)	1.4520	0.8551	2	64.5	87
$(CH_3)_2(C_2H_5)SiC\equiv CCH(C_3H_7)OH$	...	74–75 (2)	1.4428	0.8506	2	54.8	180
$(CH_3)_2(C_2H_5)SiC\equiv CCH(C_3H_7)OR^a$	...	143–144 (13)	1.4403	0.8601	*b*	...	180
$(CH_3)_2(C_2H_5)SiC\equiv CC(CH_3)_2OH$	...	88–89 (6)	1.4471	0.8570	2	...	189
$(CH_3)_2(C_2H_5)SiC\equiv CC(CH_3)(C_2H_5)OH$	...	92–95 (4)	1.4345	0.8601	2	...	172

TABLE XV (*Continued*)

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(CH_3)_2(C_2H_5)SiC\equiv CC(CH_3)(C_2H_5)OR^a$	...	120–122 (2)	1.4289	0.8626	*b*	...	172
$(CH_3)_2HSiC\equiv CCH(C_3H_7)OH$	...	65–66 (4)	1.4486	0.8635	2	...	180
$(CH_3)_2HSiC\equiv CCH(C_3H_7)OR^a$	...	136–137 (19)	1.4383	0.8701	*b*	...	180
$(CH_3)(C_2H_5)_2SiC\equiv CC(CH_3)_2OH$	...	79 (6)	1.4522	0.8614	2	...	190
$(CH_3)(C_2H_5)_2SiC\equiv CCH(C_3H_7)OH$	...	89–90 (3)	1.4498	0.8600	2	...	180
$(CH_3)(C_2H_5)_3SiC\equiv CCH(C_3H_7)OR^a$	...	144–146 (12)	1.4460	0.8680	*b*	...	180
$(CH_3)(C_2H_5)_2SiC\equiv CC(CH_3)(CH_2Cl)OH$	...	85–86 (1.5)	1.4690	0.9721	2	72.5	129
$(CH_3)(C_2H_5)_2SiC\equiv CC\underline{(CH_3)CH_2O}$	...	73.5 (1)	1.4541	0.8765	*b*	78.5	129
$(C_2H_5)_2HSiC\equiv CCH(C_3H_7)OH$	...	85–86 (4)	1.4530	0.8660	2	...	180
$(C_2H_5)_2HSiC\equiv CCH(C_3H_7)OR^a$	...	143–144 (13)	1.4454	0.8745	*b*	...	180
$(C_2H_5)_2(C_3H_7)SiC\equiv CC(CH_3)(C_2H_5)OH$	...	98–100 (4)	1.4514	0.8491	2	...	189
$(n\text{-}C_3H_7)_2HSiC\equiv CCH(C_3H_7)OH$	...	104–105 (3)	1.4550	0.8615	2	...	180
$(n\text{-}C_3H_7)_2HSiC\equiv CCH(C_3H_7)OR^a$	...	159–161 (12)	1.4471	0.8750	*b*	...	180
$(i\text{-}C_3H_7)_2HSiC\equiv CCH(C_3H_7)OH$	...	101–103 (4)	1.4533	0.8600	2	...	180
$(i\text{-}C_3H_7)_2HSiC\equiv CCH(C_3H_7)OR^a$	...	156–159 (12)	1.4470	0.8753	*b*	...	180
$(CH_3)_2(OH)SiC\equiv CC(CH_3)_2OH$	43–44	110 (6)	1.4533	...	...	...	88
$(CH_3)(C_2H_5)HSiC\equiv CC(CH_3)_2OH$	...	82.5 (18)	1.4510	0.8605	2	65	144
$(CH_3)(C_3H_7)HSiC\equiv CC(CH_3)_2OH$	...	86 (12)	1.4515	0.8568	2	66	144
$(CH_3)(C_2H_5)HSiC\equiv CCH(C_3H_7)OH$	...	71–72 (4)	1.4518	0.8641	2	...	180
$(CH_3)(C_2H_5)HSiC\equiv CCH(C_3H_7)OR^a$	...	137–138 (14)	1.4418	0.8690	*b*	...	180
$(CH_3)(C_3H_7)HSiC\equiv CCH(C_3H_7)OH$	...	80–82 (3)	1.4532	0.8642	2	...	180
$(CH_3)(C_3H_7)HSiC\equiv CCH(C_3H_7)OR^a$	...	141–142 (12)	1.4660	0.8765	*b*	...	180
$(Et_3SiCH_2CH_2)(CH_3)(C_2H_5)SiC\equiv CC(CH_3)_2OH$	...	130–132 (2)	1.4681	0.8748	2	50.2	95
$(Et_3SiCH_2CH_2)(CH_3)(C_2H_5)SiC\equiv CC(CH_3)_2OR^a$	...	147–150 (3)	1.4590	0.8716	*b*	60	95
$(Et_3SiCH_2CH_2)(CH_3)(C_3H_7)SiC\equiv CC(CH_3)_2OH$	...	138–140 (2)	1.4684	0.8716	2	45	222
$(Et_3SiCH_2CH_2)(CH_3)(C_4H_9)SiC\equiv CC(CH_3)_2OH$	...	155–157 (4)	1.4660	0.8712	2	45	222
$(Et_3SiCH_2CH_2)(CH_3)(C_6H_5)SiC\equiv CC(CH_3)_2OH$	...	175–177 (3)	1.5095	0.9330	2	41	222
$(n\text{-}Pr_3SiCH_2CH_2)(CH_3)(n\text{-}C_3H_7)SiC\equiv CC(CH_3)_2OH$	...	157–159 (5)	1.4650	0.8636	2	55.9	95
$(n\text{-}Pr_3SiCH_2CH_2)(CH_3)(n\text{-}C_3H_7)SiC\equiv CC(CH_3)_2OR^a$	...	161–163 (2)	1.4582	0.8606	*b*	55.5	95
$(Bu_3SiCH_2CH_2)(CH_3)(C_4H_9)SiC\equiv CC(CH_3)_2OH$	...	190–192 (2)	1.4620	0.8588	2	48	95
$(C_2H_5)_3SiC\equiv CC(CH_3)_2C\equiv CC(CH_3)[C(CH_3)_3]OH$	...	74–75 (7)	1.4694	0.8866	2	...	184
$(C_2H_5)_3SiC\equiv CC(CH_3)(NHCH_3)CH_2OH$	...	109 (3)	1.4685	0.8986	*b*	30	129
$(C_2H_5)_3SiC\equiv CC(CH_3)(NHC_2H_5)CH_2OH$	...	96 (1.5)	1.4665	0.8896	*b*	61.5	129
$(C_2H_5)_3SiC\equiv CC(CH_3)[NHCH(CH_3)_2]CH_2OH$	...	98–99 (2)	1.4620	0.8794	*b*	86.2	129
$(CH_3)(C_2H_5)_2SiC\equiv CC(CH_3)(NHC_2H_5)CH_2OH$	...	95–96 (3)	1.4632	0.8850	*b*	78.9	129
$(CH_3)(C_2H_5)_2SiC\equiv CC(CH_3)[N(CH_3)_2]CH_2OH$	...	87–88 (2.5)	1.4590	0.8710	*b*	90	129
$(CH_3)(C_2H_5)_2SiC\equiv CC(CH_3)[N(C_2H_5)_2]CH_2OH$	...	90–95 (1.5)	1.4570	0.8670	*b*	86.1	129
$(CH_3)(C_2H_5)HSiC\equiv CC(CH_3)[C(CH_3)_3]OH$	...	69 (2)	1.4603	0.8768	2	26	176
$(CH_3)(C_2H_5)HSiC\equiv CC(CH_3)_2OCH(CH_3)OC_4H_9$	...	119 (4)	1.4422	0.8725	2	...	176
$(CH_3)(C_2H_5)[C_6H_5(CH_3)_2SiO]SiC\equiv CC(CH_3)[C(CH_3)_3]OH$	...	106 (0.18)	1.5124	0.9842	2	...	176

[a] Butyl vinyl ether derivative obtained from the following reaction: $(CR_3)OH + CH_2{=}CHOC_4H_9 \rightarrow (CR_3)OCH(CH_3)OC_4H_9$. [b] Derived from other acetylenic compounds. [c] 3-Hydroxycyclohexyl. [d] 2-Furyl. [e] 2-Hydroxycyclohexyl.

In the case of tertiary alcohols the reaction resulted in the dehydration and formation of a vinylalkynylsilane

$$R_3SiC\equiv CC(CH_3)_2OH \longrightarrow R_3SiC\equiv CC(CH_3){=}CH_2 + H_2O$$

The esterification of tertiary alcohols can be accomplished through the interaction of the magnesium alcoholate and adipyl chloride. The dehydration of organosilicon acetylenic alcohols with potassium hydrogen sulfate or phosphorus pentoxide leads to vinylalkynylsilanes (97, 144, 167, 170, 199, 224).

$$R_3SiC\equiv CC(R)(CH_3)OH \xrightarrow{KHSO_4} R_3SiC\equiv CC(R){=}CH_2$$

Another interesting synthetic route to vinylalkynylsilanes is the reaction of alkyllithium compounds with trimethylsilyldiacetylene (89).

Numerous other acetylenic silicon compounds have been synthesized. Their physical properties are listed in the Tables XI–XIX. In spite of the large number of alkynyl compounds prepared, there is very little information on actual or potential uses. The preparation of polymeric materials with preservation of the triple bond is mentioned in two notes (89, 90). One patent claims that some compounds showed herbicidal activity (10).

C. ALKYNYLGERMANES

The synthesis of acetylenic germanium compounds (Table XX) and their physical properties are the subject of most publications in this field. From the limited amount of information available on the chemical properties of these compounds, however, it can be assumed that they are very similar to the properties

TABLE XVI

SILICON VINYLACETYLENES, $R_3SiC{\equiv}CC(R){=}CR_2$

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$Cl_3SiC{\equiv}CCH{=}CH_2$	...	76–80 (11)	1.5240[a]	...	2	...	140
$(CH_3)_3SiC{\equiv}CCH{=}CH_2$	...	52–53 (80)	1.4510	0.7714	2	...	138, 140, 224
$(CH_3)_3SiC{\equiv}CCH{=}CH(CH_3)$	...	46.5–49 (20)	1.4600	0.7811	2	51	224
$(CH_3)_3SiC{\equiv}CCH{=}C(C_2H_5)_2$	...	63–64	1.4680	0.8034	b	37	158
$(CH_3)_3SiC{\equiv}CCH{=}C(C_2H_5)(C_3H_7)$	...	72–74 (3)	1.4686	0.8076	b	42	158
$(CH_3)_3SiC{\equiv}CCH{=}C(C_2H_5)(C_3H_7\text{-}i)$	...	42–3 (0.7)	1.4681	0.8073	b	32	158
$(CH_3)_3SiC{\equiv}CCH{=}C(C_2H_5(C_4H_9)$	...	72–73 (2)	1.4687	0.8138	b	38	158
$(CH_3)_3SiC{\equiv}CC(CH_3){=}CH_2$	...	32 (15)	1.4465	0.7854	b	...	167
		32–34 (15)	1.4510	0.7854	b	...	224
		31 (12)	1.4445	0.7736	b	29	196
$(CH_3)_3SiC{\equiv}CCH{=}CH[N(CH_3)_2]$	...	63–64 (2)	1.5272	0.8541	2	40	135
$(CH_3)_3SiC{\equiv}CCH{=}CH[N(C_2H_5)_2]$	...	67–69 (2)	1.5218	0.8642	2	...	135
$(C_2H_5)_3SiC{\equiv}CCH{=}CH_2$	...	74–76 (20)	1.4695	0.8145	2	...	138, 140, 224
$(C_2H_5)_3SiC{\equiv}CC(CH_3){=}CH(CH_3)$	...	115–116 (20)	...	...	...	...	21
$(C_2H_5)_3SiC{\equiv}CC(CH_3){=}CH_2$	...	130 (755)	1.4515	0.7867	...	...	21
$(C_2H_5O)_3SiC{\equiv}CCH{=}CH_2$	...	78–79 (7)	1.4352	0.9407	2	...	140
$(C_3H_7)_3SiC{\equiv}CCH{=}CH_2$	...	87–89 (7)	1.4700	0.8173	2	...	138
$(C_4H_9)_3SiC{\equiv}CCH{=}CH_2$	...	108–110 (8)	1.4700	0.8201	2	...	138, 140
$(C_6H_5)_3SiC{\equiv}CCH{=}CH_2$	91	...	...	...	2	...	224
	93						141
$(p\text{-}ClC_6H_4)_3SiC{\equiv}CCH{=}CH_2$	107–108	...	...	...	2	...	140
$(CH_3)_2HSiC{\equiv}CC(CH_3){=}CH_2$	...	130 (755)	1.4515	0.7867	2	80	144
$(CH_3)_2C_6H_5SiC{\equiv}CCH{=}CH_2$	...	83–84 (6.5)	1.5391	0.9229	2	...	140
$(CH_3)_2(C_6H_5CH_2)SiC{\equiv}CCH{=}CH_2$	...	111–112 (11)	1.5391	0.9185	2	...	140
$(CH_3)_2(p\text{-}CH_3C_6H_4)SiC{\equiv}CCH{=}CH_2$	...	112–113.5 (10)	1.5368	0.9147	2	...	140
$(CH_3)_2(\alpha\text{-}C_{20}H_7)SiC{\equiv}CCH{=}CH_2$	...	146–147.5	1.6029	1.0116	2	...	140
$(CH_3)(C_2H_5)(H)SiC{\equiv}CCH{=}CH_2$	...	63–63.5 (79)	1.4640	0.7872	2	...	136, 154
$(CH_3)(C_2H_5)(H)SiC{\equiv}CC(CH_3){=}CH_2$	...	141 (750)	1.4581	0.7948	2	95	144
$(CH_3)(C_3H_7)(H)SiC{\equiv}CC(CH_3){=}CH_2$	...	56 (9)	1.4590	0.8007	2	75	144
$[(C_2H_5)_3SiCH_2CH_2](CH_3)(C_3H_7)SiC{\equiv}CC(CH_3){=}CH_2$	...	131–132 (4)	1.4691	0.8379	2	82	222
$[(C_2H_5)_3SiCH_2CH_2](CH_3)(C_4H_9)SiC{\equiv}CC(CH_3){=}CH_2$	...	132–134 (6)	1.4612	0.8287	2	80	222
$[(C_2H_5)_3SiCH_2CH_2](CH_3)(C_6H_5)SiC{\equiv}CC(CH_3){=}CH_2$	...	162–164 (5)	1.5160	0.90–4	2	83	222
$[(C_3H_7)_3SiCH_2CH_2](CH_3)(C_3H_7)SiC{\equiv}CC(CH_3){=}CH_2$	...	140–142 (3)	1.4730	0.8397	2	88	222
$(CH_3)_2(OH)SiC{\equiv}CCH{=}CH_2$	...	56–57 (10)	1.4800	0.8943	2	42.5	88, 195
$(CH_3)_2(OR)SiC{\equiv}CCH{=}CH_2$[c]	...	111–113 (26)	1.4511	0.8819	2	32.9	88, 195
$(CH_3)_2[O(CH_3)HCOC_3H_7]SiC{\equiv}CCH{=}CH_2$	...	71.5–73 (8)	1.4504	0.8846	2	56.4	88, 195
$(CH_3)_2(Cl)SiC{\equiv}CCH{=}CH_2$	...	53–54 (26)	1.4694	0.9570	2	53.4	88, 195
$(C_2H_5)_2(OH)SiC{\equiv}CCH{=}CH_2$	...	60–61 (12)	1.4875	0.9134	2	50	88, 195,
	...	75–76 (4)	1.4815	0.9075		20.5	201
$(C_2H_5)_2(OR)SiC{\equiv}CCH{=}CH_2$[c]	...	90–91 (9)	1.4558	0.8816	2	61.4	88, 195
$(i\text{-}C_3H_7)_2(OH)SiC{\equiv}CCH{=}CH_2$	...	86 (10)	1.4848	0.8900	2	...	88
$(CH_3)(C_2H_5)(OH)SiC{\equiv}CCH{=}CH_2$	...	62 (4.5)	1.4740	0.8908	2	41	88, 214
$(H)(C_2H_5)(OH)SiC{\equiv}CCH{=}CH_2$	...	64–65 (22)	1.4715	0.8960	2	23.2	88, 195
$[(CH_3)_3SiO](CH_3)_2SiC{\equiv}CCH{=}CH_2$	...	52 (16)	1.4424	0.8381	2	39.2	88

[a] Temperature 25°. [b] Synthesized from other acetylenic compounds. [c] Acetal derivative (see footnote in Table XV).

of the corresponding silicon compounds. The acid cleavage of substituted (phenylethynyl)triethylgermanes has been investigated.

$$XC_6H_4C{\equiv}CGe(C_2H_5)_3 + ROH \xrightarrow{H^+} XC_6H_4C{\equiv}CH + (C_2H_5)_3GeOR$$

It is assumed that the reaction involves the carbonium ion $Ar{-}C^+{=}C(H)Ge(C_2H_5)_3$ as an intermediate. The effect of the substituents X has been studied and discussed (33).

1. *Reactions of Ethynylorganogermanes, $R_{4-n}Ge(C{\equiv}CH)_n$*

Trialkylethynylgermanes have been reacted with alkylmagnesium bromides

$$R_3GeC{\equiv}CH + R'MgBr \longrightarrow R_3GeC{\equiv}CMgBr + R'H$$

These acetylenic Grignard compounds can be used to synthesize alkynylgermanes (116)

$$\begin{array}{lll} R_3GeC{\equiv}CMgBr + & & \\ CO_2 & \longrightarrow & R_3GeC{\equiv}CCOOH \text{ (unstable)} \\ BrCH_2CH{=}CH_2 & \longrightarrow & R_3GeC{\equiv}CCH_2CH{=}CH_2 \\ R'CHO & \longrightarrow & R_3GeC{\equiv}CCH(OH)R' \\ CH_3COCH_3 & \longrightarrow & R_3GeO{\equiv}CC(CH_3)_2OH \end{array}$$

TABLE XVII
BISSILICON ACETYLENES, $R_3SiC{\equiv}CSiR_3$

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$Cl_3SiC{\equiv}CSiCl_3$	...	173–174	...	...	6f	...	12
$Cl(CH_3)_2SiC{\equiv}CSi(CH_3)_2Cl$	...	113 (65)	...	...	*a*	...	39
$HO(CH_3)_2SiC{\equiv}CSi(CH_3)_2OH$	118–120	...	...	...	2	50	39, 88, 201
$Cl(CH_3)_2SiC{\equiv}CSi(CH_3)Cl_2$	...	112–116 (0.5)	1.4413	0.9950	*a*	...	88
$HO(CH_3)_2SiC{\equiv}CSi(CH_3)_3$	112, subl 90 (10)	...	...	...	2	...	88
$HO(CH_3)(C_2H_5)SiC{\equiv}CSi(CH_3)_3$	112	...	...	...	2	...	88
$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$	26	133–139	1.4259^b	0.763	2, 6c	30	39, 40, 118, 120
		136.6	1.4190	0.7516			
			1.4260	0.7703			
$(C_4H_9)_3SiC{\equiv}CSi(C_4H_9)_3$	...	216–218 (22)	1.4597	0.8276	2	...	142
$(C_6H_5)_3SiC{\equiv}CSi(C_6H_5)_3$	156 155	230–240 (10^{-4})	...	...	1b, 2	...	8, 46, 142
$(C_6H_{13})SiC{\equiv}CSi(C_6H_{13})_3$	...	303–305 (3)	1.4602	0.8354	2	...	142

[a] Synthesized from other acetylenic compounds. [b] 25°.

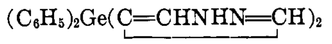
TABLE XVIII
SILICON DIACETYLENES, $R_3SiC{\equiv}CC{\equiv}CR$

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(CH_3)_3SiC{\equiv}CC{\equiv}CH$	...	40 (30)	1.466	0.7970	2	25.4	159
$(CH_3)_3SiC{\equiv}CC{\equiv}CCH_3$	...	36 (2)	1.4872	0.8195	2	...	157
$(CH_3)_3SiC{\equiv}CC{\equiv}CC_2H_5$	...	41.5 (1.5)	1.4868	0.8120	2	77	157
$(CH_3)_3SiC{\equiv}CC{\equiv}CC_3H_7$	...	66 (2)	1.4865	0.8197	2	62.7	157
$(CH_3)_3SiC{\equiv}CC{\equiv}CCH(C_2H_5)OH$	67	85 (3)	...	...	2	68	86
$(CH_3)_2(C_2H_5)SiC{\equiv}CC{\equiv}CCH(C_2H_5)OH$	38	110 (4)	1.4900	0.8874	2	56.5	86
$(CH_3)_3SiC{\equiv}CC{\equiv}CSi(CH_3)_3$	106	...	...	...	2	...	159, 169

The bromination of tetraethynylgermane yields tetrakis(1,2-dibromovinyl)germane (29, 117)

$$Ge(C{\equiv}CH)_4 + 4Br_2 \longrightarrow Ge(CBr{=}CHBr)_4$$

Diphenyldiethynylgermane forms with diazomethane the dipyrazolyl compound



$$(C_6H_5)_2Ge(C{=}CHNHN{=}CH)_2 \qquad (29)$$

Organogermanes add to trialkylethynylgermanes (123)

$$R_3GeC{\equiv}CH + HGeR_3' \longrightarrow R_3GeCH{\equiv}CHGeR_3'$$

2. *Reactions of Germanium Acetylenic Alcohols, $R_{4-n}Ge(C{\equiv}CCR_2OH)_n$*

These alcohols undergo the same transformations as the silicon-containing alcohols. The corresponding chlorides are formed with hydrogen chloride or phosphorus pentachloride (181, 183, 187). Interaction with vinyl butyl ether yields the acetal derivatives (174, 178, 183, 187), with acrylonitrile the cyanoethyl esters (187), and with acetic acid the corresponding acetate (168). Triethylchlorosilane condenses in the presence of pyridine with germanium acetylenic alcohols (187)

$$R_3GeC{\equiv}CC(CH_3)_2OH + ClSi(C_2H_5)_3 \xrightarrow{\text{pyridine}} R_3GeC{\equiv}CC(CH_3)_2OSi(C_2H_5)_3$$

The reaction of an alcohol of this type with triethylethoxygermane has also been reported (152)

$$R_3GeC{\equiv}CCH_2OH + R_3GeOC_2H_5 \xrightarrow{180\text{–}200°} R_3GeC{\equiv}CCH_2OGeR_3$$

The dehydration of a tertiary alcohol with phosphorus oxychloride resulted in the formation of a vinylethynylgermane (116).

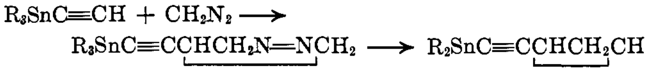
$$R_3GeC{\equiv}CC(CH_3)_2OH \xrightarrow{POCl_3} R_3GeC{\equiv}CC(CH_3){=}CH_2$$

D. ALKYNYLTIN COMPOUNDS

Many acetylenic tin compounds (Table XXI), indeed most of those reported, have been synthesized during the past 10 years. The thermal and chemical stability of the carbon–tin bond in alkynyltin compounds is considerably lower than the corresponding silicon and germanium compounds. Most reactions which have been tried result in the cleavage of the tin–carbon bond. Triphenylpropynyltin, however, has been hydrogenated in the presence of Raney nickel (103)

$$(C_6H_5)_3SnC{\equiv}CCH_3 \xrightarrow{[H]} (C_6H_5)_3SnCH_2CH_2CH_3$$

An attempt to hydrogenate trialkyl(vinylethynyl)tin was not successful (251). Triethyl(vinylethynyl)tin reacts with diazomethane to yield 3-(triethylstannylethynyl)-Δ^2-pyrazoline, which upon heating gives (triethylstannylethynyl)cyclopropane (253)



$$R_3SnC{\equiv}CH + CH_2N_2 \longrightarrow R_3SnC{\equiv}CCHCH_2N{=}NCH_2 \longrightarrow R_2SnC{\equiv}CCHCH_2CH$$

TABLE XIX

$R_3SiC{\equiv}CXC{\equiv}CSiR_3$ AND $RC{\equiv}CSi(R_2)XSi(R_2)C{\equiv}CR$

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(CH_3)_3SiCC{\equiv}CCH_2OCH_2C{\equiv}CSi(CH_3)_3$	...	121 (13)	1.4605	...	*a*	90	15
$Cl_3CCH[OC(CH_3)_2C{\equiv}CSi(CH_3)_3]_2$	26–27	86–88 (4)	1.4568	1.0021	*a*	...	179
$(CH_2)_4[CO_2(CH_3)_2C{\equiv}CSi(C_2H_5)_3]_2$	131	198 (2)	...	...	*a*	18	196
$S[CH(CH_3)C{\equiv}CSi(CH_3)_3]_2$	...	115–116 (8)	1.4945	0.8924	*a*	30	87
$O_2S[CH(CH_3)C{\equiv}CSi(CH_3)_3]_2$	60	...	...	...	*a*	80.2	87
$S[CH(CH_3)C{\equiv}CSi(CH_3)(C_2H_5)]_2$	...	113 (2)	1.5085	0.9187	*a*	39	87
$O_2S[CH(CH_3)C{\equiv}CSi(CH_3)(C_2H_5)]_2$	79	...	...	...	*a*	78.5	87
$HC{\equiv}CSi(C_2H_5)_2CH_2CH_2Si(C_2H_5)_2C{\equiv}CH$	...	89–91 (3)	1.4600	0.8418	2	...	98
$HC{\equiv}CSi(C_2H_5)_2CH_2CH_2Si(CH_3)(CH_2CHMe_2)C{\equiv}CH$	...	102–104 (3)	1.4620	0.8519	2	...	98
$p\text{-}C_6H_4[Si(CH_3)_2C{\equiv}CH]_2$	52	80–82 (2)	...	...	2	...	98
$p\text{-}C_6H_4[Si(C_2H_5)_2C{\equiv}CH]_2$	...	152–154 (4)	1.5180	0.9432	2	...	98
$[(HC{\equiv}C)_3Si]_2O$	19–20	...	...	...	2	...	235
$[CH_3(CH_2)_2C{\equiv}CSi(CH_3)(OH)]_2O$	...	...	...	...	*a*	...	39
$[CH_3(CH_2)_3C{\equiv}CSi(CH_3)(OH)]_2O$	...	...	...	...	*a*	...	39
$[(CH_2{=}CHC{\equiv}C)(CH_3)_2Si]_2O$	...	98.5–100.5 (12)	1.4730	0.8911	*a*	33.3	195
		85–87 (5)	1.4721	0.8909		...	214
		74 (1)	0.4730	0.8911		...	88
$[(CH_2{=}CHC{\equiv}C)(C_2H_5)_2Si]_2O$	...	109–110 (4)	1.4931	0.9120	*a*	...	88
$p\text{-}C_6H_4[Si(CH_3)_2C{\equiv}CC(CH_3){=}CH_2]_2$	46–47	158–160 (0.013)	1.5310	0.9592	*a*	60	97
$p\text{-}C_6H_4[Si(C_2H_5)_2C{\equiv}CC(CH_3){=}CH_2]_2$	...	138–160 (0.013)	1.5335	...	*a*	60	97
$p\text{-}C_6H_4[Si(CH_3)_2C{\equiv}CC(CH_3){=}CHC_3H_7]_2$	...	145–147 (0.013)	1.5260	0.9189	*a*	60	97
$p\text{-}C_6H_4[Si(C_2H_5)_2C{\equiv}CC(CH_3){=}CHC_3H_7]_2$	...	150–152 (0.013)	1.5230	0.9294	*a*	70	97
$(CH_3)_2Si[OSi(CH_3)_2C{\equiv}CCH{=}CH_2]_2$	...	99 (8)	1.4616	0.9192	*a*	23.5	88
$H(CH_3)Si[OSi(CH_3)_2C{\equiv}CCH{=}CH_2]_2$	...	80 (1.5)	1.4629	0.9107	*a*	35.8	88
$[(C_2H_5)_3SiC{\equiv}CC(CH_3)CH_2OH]_2NCH_3$	...	170 (2)	1.4775	0.9131	*a*	58	129
$[(C_2H_5)_3SiC{\equiv}CC(CH_3)CH_2OH]_2NC_2H_5$	...	147 (1)	1.4800	0.9159	*a*	27	129
$[(CH_3)(C_2H_5)_2SiC{\equiv}CC(CH_3)CH_2OH]_2NC_2H_5$	...	145 (2)	1.4795	0.9208	*a*	60	129
$p\text{-}C_6H_4[Si(CH_3)_2C{\equiv}CC(CH_3)_2OH]_2$	100–103	...	...	...	*a*	43	97, 98
$p\text{-}C_6H_4[Si(C_2H_5)_2C{\equiv}CC(CH_3)(C_2H_5)OH]_2$	...	158–160 (0.013)	1.5226	...	*a*	50	97
$p\text{-}C_6H_4[Si(CH_3)_2C{\equiv}CC(CH_3)(C_4H_9)OH]_2$	...	170–172 (0.013)	1.5125	...	*a*	49	97
$p\text{-}C_6H_4[Si(C_2H_5)_2C{\equiv}CC(CH_3)(C_4H_9)OH]_2$	...	182–184 (0.013)	1.5130	...	*a*	...	97
$p\text{-}C_6H_4[SiMe_2C{\equiv}CC(C_2H_5)_2OH]_2$	...	158–160 (0.013)	1.5230	...	*a*	...	98

[a] Synthesized from other acetylenic compounds.

Bis(trialkyltin)diacetylenes react with triaryltin halides to form bis(triaryltin)diacetylenes in good yields (65)

$$(CH_3)_3SnC{\equiv}CC{\equiv}CSn(CH_3)_3 + 2(C_6H_5)_3SnCl \longrightarrow (C_6H_5)_3SnC{\equiv}CC{\equiv}CSn(C_6H_5)_3 + 2(CH_3)_3SnCl$$

This interesting method can also be used to prepare other organometallic diacetylenes

$$(CH_3)_3SnC{\equiv}CC{\equiv}CSn(CH_3)_3 + 2(C_6H_5)_2AsCl \longrightarrow (C_6H_5)_2AsC{\equiv}CC{\equiv}CAs(C_6H_5)_2 + 2(CH_3)_3SnCl.$$

E. ALKYNYLLEAD COMPOUNDS

No reactions of acetylenic lead compounds (Table XXII) are reported. Many of these compounds hydrolyze rapidly. Some are reported to be light sensitive (55). Disubstituted lead diacetylides exhibit improved hydrolytic stability (63).

IV. ALKYNYL COMPOUNDS OF THE FIFTH GROUP ELEMENTS

Although the nitrogen compounds are not included in this review, one recent publication which deals with the synthesis and properties of acetylenic amines should be noted (31). Organophosphorus compounds are generally not thought of as metal organic compounds; however, the similarity of the properties of phosphorus and arsenic acetylenic compounds justifies their discussion here.

A. PREPARATIVE METHODS

The reaction of acetylenic Grignard reagents with halides and organo-substituted group V element halides is the most frequently used method for the synthesis of the corresponding alkynyl compounds. Trialkynylphosphines have been obtained from the interaction of bisalkynylmercury compounds with phosphorus tribromide (28)

$$3(RC{\equiv}C)_2Hg + 2PBr_3 \longrightarrow 2(RC{\equiv}C)_3P + 3HgBr_2$$

The corresponding diacetylenes were prepared in a similar manner (62)

$$3(RC{\equiv}CC{\equiv}C)_2Hg + 2PI_3 \longrightarrow 2(RC{\equiv}CC{\equiv}C)_3P + 3HgI_2$$

This method could probably be extended to other elements of this group as well as those of the fourth group elements. A similar reaction between bis(di-

TABLE XX
ALKYNYLGERMANIUM COMPOUNDS

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
A. $Ge(C\equiv CR)_4$							
$Ge(C\equiv CH)_4$	90–91, 94				1b, 2	...	29, 117
$Ge(C\equiv CC_6H_5)_4$	187–188				1b	...	16
$Ge(C\equiv CC_6H_4Br\text{-}p)_4$	266				1b	49	67
$Ge(C\equiv CC_6H_{11})_4$	146				1b	31.5	66
B. $RGe(C\equiv CR)_3$							
$CH_3Ge[C\equiv CC(CH_3)_2OH]_3$	208				2	48	168
$C_2H_5Ge[C\equiv CC_6H_5]_3$	71–72.5				1b	...	89
$C_6H_5Ge[C\equiv CC_6H_5]_3$	108–109				1b	52.5	64
$CH_3Ge[C\equiv CC(CH_3)(C_2H_5)OH]_3$	165–167				2	...	182
$CH_3Ge[C\equiv CC(C_2H_5)_2OH]_3$	146–147				2	...	182
$C_2H_5Ge[C\equiv CC(CH_3)_2OH]_3$	171				2	...	182
$C_2H_5Ge[C\equiv CC(C_2H_5)(CH_3)OH]_3$	152–153				2	...	182
C. $R_2Ge(C\equiv CR)_2$							
$(C_4H_9)_2Ge(C\equiv CH)_2$	...	46 (0.5)	...	...	1b	...	29
$(C_6H_5)_2Ge(C\equiv CH)_2$	49	...	...	...	1b	...	29
$(C_2H_5)(C_6H_5)Ge(C\equiv CH)_2$	...	No data	...	...	2	...	90
$(C_2H_5)_2Ge(C\equiv CC_4H_9)_2$	...	98 (0.15)	1.4729^a	0.981^a	2	63	71
$(C_2H_5)_2Ge(C\equiv CC_6H_5)_2$	...	139–140 (0.01)	1.5982^a	1.129^a	2	64	71
		191–193 (2)	1.5935^a	...	1b	72.5	64
$(i\text{-}C_3H_7)_2Ge(C\equiv CC_6H_5)_2$	...	205 (2)	1.5840^b	...	1b	40	64
$(C_6H_5)_2Ge(C\equiv CC_3H_7)_2$	...	136 (0.01)	1.5702	1.188	2	67	71
$(C_6H_5)_2Ge(C\equiv CC_6H_5)_2$	82.5–83.5	...	...	...	1b	58	64
$(CH_3)_2Ge[C\equiv CC(CH_3)_2OH]_2$	97	...	...	...	2	50	168
$(CH_3)_2Ge[C\equiv CC(CH_3)_2OAc]_2$	54	142–143 (7)	...	...	*c*	...	168
$(CH_3)_2Ge[C\equiv CC(CH_3)(C_2H_5)OH]_2$	82–83	...	...	...	2	48.3	178
$(CH_3)_2Ge[C\equiv CC(CH_3)(C_2H_5)OAc]_2$	43–44	...	...	...	*c*	53.2	178
$(C_2H_5)_2Ge[C\equiv CC(CH_3)_2OH]_2$	56–57	...	...	...	2	47.5	178, 182
$(C_2H_5)_2Ge[C\equiv CC(CH_3)_2OAc]_2$	31–32	...	...	...	*c*	...	178
$(C_2H_5)_2Ge[C\equiv CC(CH_3)(C_2H_5)OH]_2$	45–47	...	...	...	2	...	178
D. $R_3GeC\equiv CR$							
$(C_2H_5)_3GeC\equiv CH$	...	71 (65)	1.4485	1.0241	2, 6f	...	99, 115
$(C_4H_9)_3GeC\equiv CH$	...	106 (2.5)	1.4581	0.9602	2, 6f	...	99, 115
$(C_6H_5)_3GeC\equiv CH$	...	...	...	...	1b	...	29
$(C_2H_5)_3GeC\equiv CC(CH_3)_2Cl$	...	65–67 (2)	1.4533	1.0484	*c*	70.5	181
$(C_2H_5)_3GeC\equiv CC(CH_3)(C_2H_5)Cl$	...	70–71 (2)	1.4560	1.0600	*c*	70	185
$(C_2H_5)_3GeC\equiv CC(CH_3){=}CH_2$	...	97 (23)	1.4792	1.0068	2	75	116, 226
$(C_2H_5)_3GeC\equiv CC_6H_5$	...	115 (1.5)	1.5360^d	...	1b, 2	92	33
		139–140 (2)	1.5391^b			59	64
$(C_2H_5)_3GeC\equiv CC_6H_4CH_3\text{-}p$	...	147 (5.8)	1.5375^d	...	1b, 2	84	33
$(C_2H_5)_3GeC\equiv CC_6H_4CH_3\text{-}o$	...	119 (1.9)	1.5330^d	...	1b, 2	80	33
$(C_2H_5)_3GeC\equiv CC_6H_4CH_3\text{-}m$	...	115 (1.2)	1.5336^d	...	1b, 2	82	33
$(C_2H_5)_3GeC\equiv CC_6H_4(C_4H_9\text{-}n)\text{-}p$	...	147 (1.9)	1.5290^d	...	1b, 2	88	33
$(C_2H_5)_3GeC\equiv CC_6H_3(CH_3\text{-}o)(CH_3\text{-}p)$	...	132 (1.8)	1.5291^d	...	1b, 2	80	33
$(C_2H_5)_3GeC\equiv CC_6H_2(CH_3\text{-}2,4,6)_3$	...	128 (0.2)	1.5330^d	...	1b, 2	92	33
$(C_2H_5)_3GeC\equiv CC_6H_4OCH_3\text{-}o$	...	138 (2)	1.5300^d	...	1b, 2	84	33
$(C_2H_5)_3GeC\equiv CC_6H_4OCH_3\text{-}m$	...	140 (2)	1.5390^d	...	1b, 2	86	33
$(C_2H_5)_3GeC\equiv CC_6H_4OCH_3\text{-}p$	...	135 (1.2)	1.5450^d	...	1b, 2	90	33
$(C_2H_5)_3GeC\equiv CC_6H_4Cl\text{-}o$	...	138 (2.8)	1.5451^d	...	1b, 2	88	33
$(C_2H_5)_3GeC\equiv CC_6H_4Cl\text{-}m$	...	128 (1.2)	1.5430^d	...	1b, 2	95	33
$(C_2H_5)_3GeC\equiv CC_6H_4Cl\text{-}p$	...	118 (0.9)	1.5466^d	...	1b, 2	86	33
$(C_2H_5)_3GeC\equiv CC_6H_4Br\text{-}o$	...	138 (1.5)	1.5570^d	...	1b, 2	78	33
$(C_2H_5)_3GeC\equiv CC_6H_4Br\text{-}m$	...	116 (0.3)	1.5580^d	...	1b, 2	85	33
$(C_2H_5)_3GeC\equiv CC_6H_4Br\text{-}p$	...	139 (1.5)	1.5612^d	...	1b, 2	86	33
$(C_2H_5)_3GeC\equiv CC_6H_3F\text{-}p$	...	106 (1.6)	1.5188^d	...	1b, 2	90	33
$(C_2H_5)_3GeC\equiv CC_6H_4I\text{-}p$	...	160 (1.8)	1.5882^d	...	1b, 2	78	33
$(C_2H_5)_3GeC\equiv CC_6H_4CF_3\text{-}m$	...	112 (2.6)	1.4898^d	...	1b, 2	90	33
$(n\text{-}C_3H_7)_3GeC\equiv CC_6H_5$	...	147–149 (4)	1.5274^b	...	1b	46	64
$(n\text{-}C_4H_9)_3GeC\equiv CC_3H_7$	...	117 (0.5)	1.4645	0.9425	2	69	99, 114
$(n\text{-}C_4H_9)_3GeC\equiv CC_4H_9$	...	131–132 (0.7)	1.4648	0.9381	2	71	114
$(n\text{-}C_4H_9)_3GeC\equiv CC_6H_5$	...	150 (1.4)	1.5195	1.0078	1b, 3	62	64, 153
		153 (2)	1.5110^b				

TABLE XX (*Continued*)

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(n\text{-}C_4H_9)_3GeC{\equiv}CC(CH_3)_2Cl$	...	95–96 (0.3)	1.4810	1.0295	*c*	...	187
$(n\text{-}C_4H_9)_3GeC{\equiv}CC(CH_3)(C_2H_5)Cl$	...	105–106 (13)	1.4840	0.9995	*c*	...	187
$(n\text{-}C_4H_9)_3GeC{\equiv}CCH_2CH{=}CH_2$	...	95 (0.2)	1.4723	0.9582	*c*	...	116
$(n\text{-}C_4H_9)_3GeC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3){=}CH_2$	...	115–116 (1)	1.4800	0.9805	2	32.5	184
$(C_6H_{11})_3GeC{\equiv}C_6H_5$	102	...	...	...	1b	66	64
$(C_6H_5)_3GeC{\equiv}CC_6H_5$	89	...	...	...	1b	82	64
$(C_2H_5)_3GeC{\equiv}C(CH_2)_3Ge(C_2H_5)_3$	...	140 (0.8)	1.4815	1.0780	2	...	117
$(C_2H_5)_3GeC{\equiv}CCH_2OGe(C_2H_5)_3$	...	173 (15)	1.4789	1.1351	*c*	...	152
$(C_2H_5)_3GeC{\equiv}CCH{=}CH_2$	...	62–63 (5)	1.4850	1.0333	2	72	226
$(C_2H_5)_3GeC{\equiv}CCH{=}CH(CH_3)$	...	78–79 (5)	1.4950	1.0173	2	80	226
$(CH_3)_3GeC{\equiv}(CH_3)_2OH$	30	72–73 (7)	...	...	2	45	99, 168
$(CH_3)_3GeC{\equiv}CC(CH_3)(C_2H_5)OH$	...	67–69 (4)	1.4355	1.0150	2	...	178, 143
$(CH_3)_3GeC{\equiv}CC(CH_3)(C_2H_5)OR^a$	...	123–124 (12)	1.431	0.9640	*c*	...	178
$(C_2H_5)_3GeC{\equiv}CCH_2OH$	...	94 (3)	1.4681	1.1172	...	...	99, 116
			1.4825	1.1172	...	...	
		107–108	1.4739	1.1100	2	...	174
		112 (9)	1.4822	1.1150	...	67	32
$(C_2H_5)_3GeC{\equiv}CCH_2OR^e$	...	146–148	1.4519	1.1130	*c*	...	174
$(C_2H_5)_3GeC{\equiv}CCH(C_3H_7)OH$	...	106 (1)	1.4722	1.0355	...	...	99, 116
		110–111	1.4660	1.0106	2	...	174
$(C_2H_5)_3GeC{\equiv}CCH(C_3H_7)OR^e$	...	152–153	1.4600	1.0230	*c*	...	174
$(C_2H_5)_3GeC{\equiv}CC(CH_3)_2OH$	...	80 (1)	1.4686	1.0183	2	...	99
	...	90–92 (5)	1.4670	1.0670	2	...	178
$(C_2H_5)_3GeC{\equiv}CC(CH_3)_2OR^e$	...	138–139 (13)	1.4598	1.0100	*c*	...	178
$(C_2H_5)_3GeC{\equiv}CC(CH_3)(C_2H_5)OH$	...	95–97 (3)	1.4690	1.0350	2	42.5	178
$(C_2H_5)_3GeC{\equiv}CC(CH_3)(C_2H_5)OR^e$	...	141–143 (12)	1.4610	0.9960	*c*	60.5	178
$(C_2H_5)_3GeC{\equiv}CC(C_2H_5)_2OH$	...	105–107 (2)	1.4713	1.0380	2	...	178
$(C_2H_5)_3GeC{\equiv}CC(C_2H_5)_2OR^e$	...	151–153 (14)	1.4658	1.0200	*c*	...	178
$(C_4H_9)_3GeC{\equiv}CC(CH_3)_2OH$	...	107–108 (0.3)	1.4705	0.9960	2	36.6	187
$(C_4H_9)_3GeC{\equiv}CC(CH_3)_2OR^e$	...	126–127 (1)	1.4625	0.9595	*c*	...	187
$(C_4H_9)_3GeC{\equiv}CC(CH_3)_2OCH_2CH_2CN$	...	132–133 (0.1)	1.4795	1.0304	*c*	52.2	187
$(C_4H_9)_3GeC{\equiv}CC(CH_3)_2OSi(C_2H_5)_3$	...	150–151 (2)	1.4590	0.9083	*c*	28	187
$(C_4H_9)_3GeC{\equiv}CC(CH_3)(C_2H_5)OH$	...	115–116 (3)	1.4785	0.9905	2	...	187
$(C_4H_9)_3GeC{\equiv}CC(CH_3)(C_2H_5)OR^e$	...	144–145 (0.2)	1.4505	0.9415	*c*	...	187
$(C_2H_5)_3GeC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OH$	...	99–100 (3)	1.4700	1.0005	*c*	...	181
$(C_2H_5)_3GeC{\equiv}CC(CH_3)_2C{\equiv}CC(CH_3)_2OR^e$	...	152–154 (3)	1.4680	1.0140	*c*	40.5	181
$(C_2H_5)_3GeC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)_2OH$	...	105–107 (3)	1.4740	1.0027	*c*	62	185
$(C_2H_5)_3GeC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)(C_2H_5)OH$	...	111 (3)	1.4770	1.0040	*c*	...	185
$(C_2H_5)_3GeC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)(C_2H_5)OR^e$	...	158–160 (3)	1.4710	1.0020	*c*	41	185
$(C_4H_9)_3GeC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)_2OH$	...	125–126 (5)	1.4917	1.0038	*c*	27	184
$(C_4H_9)_3GeC{\equiv}CC(CH_3)(C_2H_5)C{\equiv}CC(CH_3)_2O(CH_2)_2CN$	...	103–104 (0.3)	1.4962	1.0267	*c*	38.2	184
E. $R_3GeC{\equiv}CGeR_3$							
$(C_2H_5)_3GeC{\equiv}CGe(C_2H_5)_3$	...	50 (14)	...	...	1b, 2	..	53
$(C_6H_{11})_3GeC{\equiv}CGe(C_6H_{11})_3$	158	...	...	...	1b, 2	...	53
$(C_6H_5)_3GeC{\equiv}CGe(C_6H_5)_3$	127	...	...	...	1b, 2	...	53, 29
$HC{\equiv}C(C_4H_9)_2GeC{\equiv}CGe(C_4H_9)_2C{\equiv}CH$	...	130 (0.5)	...	...	1b	5.3	29
F. $R_3GeC{\equiv}CC{\equiv}CR$							
$(C_2H_5)_3GeC{\equiv}CC{\equiv}CC_2H_5$	...	118 (5)	1.5116	1.0320	2	...	99, 116
$(C_6H_5)_3GeC{\equiv}CC{\equiv}CGe(C_6H_5)_3$	294	...	...	...	1b	...	59

[a] Temperature 21°. [b] Temperature 19°. [c] Synthesized from other acetylene compound. [d] Temperature 25°. [e] Acetal derivative (see footnote *b*, Table XV).

alkyltin)diacetylide and organo-substituted arsenic halides has already been mentioned (65).

Dialkylphosphorus acetylides can also be obtained from metalated acetylenes and dialkyl(ethylthio)- or dialkylethoxyphosphines in liquid ammonia (236)

$$R'C{\equiv}CNa + C_2H_5SPR_2 \longrightarrow R'C{\equiv}CPR_2 + C_2H_5SNa$$

The esters of alkynylphosphonic acids $(RO)_2P(O)\text{-}C{\equiv}CR$ and their preparation will be discussed separately.

B. ALKYNYLPHOSPHINES

Many alkynylphosphines (Table XXIII) have been reported and their chemical behavior investigated.

TABLE XXI
ALKYNYLTIN COMPOUNDS

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield %	Ref
	A. $Sn(C{\equiv}CR)_4$						
$Sn(C{\equiv}CH)_4$	...	...	...	...	1b	>90	79
$Sn(C{\equiv}CCH_3)_4$	150	...	...	...	1b	73	103, 108
	139					65	
$Sn(C{\equiv}CC_6H_5)_4$	174 dec	...	...	...	1b, 2	...	56
$Sn(C{\equiv}CC_6H_{11})_4$	130	...	...	...	1b	44.3	66
$Sn(C{\equiv}C_6H_4Cl)_4$	161	...	...	...	1b	56.8	67
$Sn(C{\equiv}CC_6H_4Br)_4$	170	...	...	...	1b	53	67
	B. $RSn(C{\equiv}CR)_3$						
$n\text{-}C_4H_9Sn(C{\equiv}CC_6H_5)_3$	70	...	...	...	1b	63	64
$C_6H_5Sn(C{\equiv}CC_6H_5)_3$	105	...	...	...	1b	47	64
	C. $R_2Sn(C{\equiv}CR)_2$						
$(C_2H_5)_2Sn(C{\equiv}CH)_2$	...	32–35 (0.1)	...	...	1b	...	79
$(C_3H_7)_2Sn(C{\equiv}CH)_2$	...	79 (2)	1.4785	1.1819	2	34.5	219
$(C_4H_9)_2Sn(C{\equiv}CH)_2$	...	No data	...	...	2	...	90
$(CH_3)_2Sn(C{\equiv}CC_6H_5)_2$	...	96 (0.2)	1.5668[a]	...	2	65	102
$(C_2H_5)_2Sn(C{\equiv}CCH_3)_2$	...	62 (1)	1.4977	1.2332	2	66	219
$(C_2H_5)_2Sn(C{\equiv}CC_3H_7)_2$	...	66 (0.1)	1.4969	1.225	2	65	71
$(C_2H_5)_2Sn(C{\equiv}CC_4H_9)_2$	...	101 (0.15)	1.4888	1.118	2	63	71
$(C_2H_5)_2Sn(C{\equiv}CC_6H_5)_2$	...	oil	1.5919	...	2	...	71
$(C_3H_7)_2Sn(C{\equiv}C(C_3H_7)_2$	...	96 (0.15)	1.4881	1.143	2	66	71
$(C_3H_7)_2Sn(C{\equiv}CC_4H_9)_2$	...	109–110 (0.15)	1.4899	1.137	2	65	71
$(C_3H_7)_2Sn(C{\equiv}CC_6H_5)_2$	...	Oil	1.5991	...	2	...	71, 219
		135 (.09) with polymerization	1.5991				
$(C_4H_9)_2Sn(C{\equiv}CC_3H_7)_2$	...	99 (0.1)	1.4884	1.249	2	68	71
$(C_4H_9)_2Sn(C{\equiv}CC_4H_9)_2$	...	114 (0.15)	1.4827	1.063	2	72	71
$(C_4H_9)_2Sn(C{\equiv}CC_6H_5)_2$	...	Oil	1.5878	...	2	...	71
$(C_6H_5)_2Sn(C{\equiv}CC_4H_9)_2$	...	Oil	1.6048	...	2	...	71
$(C_6H_5)_2Sn(C{\equiv}CC_6H_5)_2$	71–72	...	...	...	2	71	71
$(C_2H_5)_2Sn(C{\equiv}CCH{=}CH_2)_2$	...	96 (1)	1.5428	1.2267	2	70	219
$(C_3H_7)_2Sn(C{\equiv}CCH{=}CH_2)_2$	...	102 (1)	1.5343	1.1840	2	...	219
$(C_4H_9)_2Sn(C{\equiv}CCH{=}CH_2)_2$	...	108 (1)	1.5188	1.1352	2	...	219
	D. $R_3SnC{\equiv}CR$						
$(CH_3)_3SnC{\equiv}CH$	...	95–96	...	...	2	15	103
		98, 58 (150)	1.4626	1.3602	3	65	220
$(C_2H_5)_3SnC{\equiv}CH$	...	49–50 (15)	1.4770	1.2458	3	...	220
		60 (15)	1.4770	1.2455			205
		57–58 (11)			1b	80	79
$(C_3H_7)_3SnC{\equiv}CH$	...	67 (2)	1.4780	1.1545	3	...	220
		91 (10)	1.4780	1.1555	...	...	205
$(C_4H_9)_3SnC{\equiv}CH$	...	98–99 (2.5)	1.4765	1.1038	...	...	220
		85–90 (0.1)			1b, 3		79
		100–101 (3)	1.4767	1.1034	...	...	205
$(C_6H_5)_3SnC{\equiv}CH$	34	...	...	...	1a, 2	70	52
	35–36						103
$(CH_3)_3SnC{\equiv}CBr$	...	67–68 (14)	1.5175	1.7396	4	...	255
$(C_6H_5)_3SnC{\equiv}CCl$	80–81	...	...	...	1a	80	230
$(C_6H_5)_3SnC{\equiv}CBr$	104–105	...	...	...	4	75	103
$(CH_3)_3SnC{\equiv}CCH_3$	...	25–26 (0.2)	...	...	2	50	103
$(CH_3)_3SnC{\equiv}CCH(CH_3)_2$	...	50 (10)	1.4676	1.2076	4	...	134
$(CH_3)_3SnC{\equiv}CC_3H_7$	...	172 (760)	...	...	3	...	83
$(CH_3)_3SnC{\equiv}CC_4H_9$	...	82 (12)	...	...	3	...	83
$(CH_3)_3SnC{\equiv}CC_6H_5$	...	68 (0.3)	...	...	3	95	83
	...	107 (1.5)	...	...	2, 4	40	103
	...	87–88 (2)	1.5720	1.3324	...	...	134
$(CH_3)_3SnC{\equiv}CC_5H_7$[b]	...	68–70 (3)	...	...	2, 4	20	102
$(CH_3)_3SnC{\equiv}CC_6H_9$[c]	...	68–70 (3)	...	...	2	20	103
$(C_2H_5)_3SnC{\equiv}CCH_3$	...	40 (1)	1.4866	1.2273	1a	...	133
$(C_2H_5)_3SnC{\equiv}CCH(CH_3)_2$	...	91.5 (10)	1.4778	1.1478	4	...	134
$(C_2H_5)_3SnC{\equiv}C\underbrace{CHCH_2CH_2}$	...	76–77 (1)	1.5041	1.2155	*d*	...	253

TABLE XXI (*Continued*)

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$CH_3(C_2H_5)_2SnC\equiv C\underbrace{CHCH_2CH_2}$	...	83–85 (1.5–2)	1.4948	1.1737	*d*	...	253
$(C_2H_5)_3SnC\equiv CC_3H_5N_2^{e}$	...	Oil	1.5469	1.339	*d*	...	253
$(C_2H_5)_3SnC\equiv CC_6H_4OCH_3$	...	119 (0.18)	...	...	5	90	126
$(C_2H_5)_3SnC\equiv CCH{=}CHOCH_3$	...	138 (13)	...	...	5	82	126
$(C_2H_5)_3SnC\equiv CCN$	47	126 (15)	...	...	5	83	126
$(C_2H_5)_3SnC\equiv CC_6H_5$	...	120–122 (2)	1.5558	1.2462	1a, 2–5	75	208, 213 215, 216 126, 134 51, 83, 105
$(C_3H_7)_3SnC\equiv CC_6H_5$	...	151 (1)	1.5388	1.1811	5	...	220
$(C_4H_9)_3SnC\equiv CC_6H_5$	...	150 (1)	1.5270	1.1317	2, 3, 6a	74	104, 126
	...	184 (1–2)	1.5315	...	...	89.5	208
$(C_6H_5)_3SnC\equiv CCH_3$	74–75	...	...	...	2	85	101, 103
	43	...	...	...	...	...	52
$(C_6H_5)_3SnC\equiv CCH_2OH$	66–68	...	...	...	2	80	103
$(C_6H_5)_3SnC\equiv CC_6H_5$	62	...	...	...	1a, 2, 3, 6a	80	51, 83, 101 103, 104, 126
$(C_6H_5)_3SnC\equiv CC_6H_4Br\text{-}p$	128	...	...	...	2	36	103
$(C_6H_5)_3SnC\equiv CC_6H_9^{c}$	64	...	...	...	2, 4	77	102
	105–106	...	...	...	...	66	103
$(C_6H_5)_3SnC\equiv CCH_2C_{14}H_9^{b}$	150	...	...	...	2	70	103
$(p\text{-}ClC_6H_4)_3SnC\equiv CC_6H_5$	132	...	...	...	1a, 2	...	51
$[1,4(CH_3)_2C_6H_4]_3SnC\equiv C_6H_5$	106	...	...	...	1a, 2	...	51
$(C_6H_5)_3SnC\equiv CCH(OC_2H_5)_2$	58–60	...	...	...	1a, 2	...	81
$(C_2H_5)_3SnC\equiv CCH_2OCH_3$	...	62–63 (0.55)	1.4878	1.2404	5	25.6	206
$(C_2H_5)_3SnC\equiv CC(CH_3)_2OCH_3$	...	58–59 (0.4)	1.4759	1.1669	*d*	30.7	218
$(C_2H_5)_3SnC\equiv CCH_2CH_2OCH{=}CH_2$	...	107.5–108 (2)	1.4925	1.1993	5	56.3	206
$(C_2H_5)_3SnC\equiv CCH_2OR^{g}$	...	105 (0.32)	1.4754	1.1474	2, 5	53.4	202, 205
	...	142 (5)	1.4775	1.1363	...	...	211
$(C_2H_5)_3SnC\equiv CCH_2CH_2OR^{g}$	...	111–112 (0.3)	1.4749	1.1290	2, 5	52.2	202, 203 205, 211
$(C_2H_5)_3SnC\equiv CCH(CH_3)OR^{g}$	...	120 (2)	1.4722	1.1075	...	...	202, 205
	...	104 (0.45)	1.4697	1.1176	2, 5	...	211, 220
$(C_2H_5)_3SnC\equiv CC(CH_3)_2OR^{g}$	...	112 (1.5)	1.4670	1.0727	...	...	205, 211,
		102 (0.37)	1.4680	1.1010	2, 5	...	220
$(C_2H_5)_3SnC\equiv CCH_2OSn(C_2H_5)_3$	...	160 (5)	1.5145	1.3541	5	...	220
		124–125 (1)	1.5128	1.3751	...	...	213
$(C_2H_5)_3SnC\equiv CCH_2CH_2OSn(C_2H_5)_3$	...	134–135 (1)	1.5086	1.3412	5	75.4	213
$(C_2H_5)_3SnC\equiv CCH(CH_3)OSn(C_2H_5)_3$	...	138 (2)	1.5005	1.2969	5	...	220
		111–112 (0.5)	1.5039	1.3313	...	43.4	213
$(C_2H_5)_3SnC\equiv CC(CH_3)_2OSn(C_2H_5)_3$	...	113–114 (0.5)	1.4987	1.3006	5	23	213
$(C_3H_7)_3SnC\equiv CCH(CH_3)OSn(C_3H_7)_3$	...	165 (1)	1.4970	1.2139	5	...	220
$(C_3H_7)_3SnC\equiv CC(CH_3)_2OSn(C_3H_3)_3$	...	172 (4)	1.4925	1.2073	5	...	220
$(C_4H_9)_3SnC\equiv CCH(CH_3)OSn(C_4H_9)_3$	...	200 (3)	1.4875	1.1558	5	...	220
$(C_4H_9)_3SnC\equiv CC(CH_3)_2OSn(C_4H_9)_3$	...	198 (2)	1.4890	1.1277	5	...	220
E. $R_3SnC\equiv CC(R){=}CR_2$							
$(CH_3)_3SnC\equiv CCH{=}CH_2$	...	46.5–47 (10)	1.5067	1.3066	2	25	130
	...	47–48 (10)	1.5067	1.3103	4	18	251
	...	49 (10)	1.5058	1.3072	4	80	134
$(CH_3)_3SnC\equiv C(CH_3){=}CH_2$	...	40–42 (5)	...	...	...	30	103
	...	57–58 (5)	1.5013	1.2499	2, 4	37	251
	...	40–42 (5)	1.4958	...	...	30	102
$(CH_3)_3SnC\equiv CCH{=}CH_2CH_3$	...	65–67 (10)	1.5088	1.2771	4	44	251
$(C_2H_5)_3SnC\equiv CCH{=}CH_2$	...	78 (3)	1.5085	1.2180	...	...	205
	...	89.5–90 (10)	1.5098	1.2181	...	30, 85	130, 251, 252
	...	89.5–90 (10)	1.5092	1.2230	2, 4	...	249
	...	90–91 (10)	1.5100	1.2183	...	...	134
	...	53 (1)	1.5073	1.2165	...	87	208
$(C_2H_5)_3SnC\equiv CCH{=}CHN(C_2H_5)_2$	...	125–126 (1.5)	1.5470	1.648	1b, 5	...	220
$(C_2H_5)_3SnC\equiv CCH{=}CHOC_4H_9$	...	107–108 (0.5)	1.5098	1.1760	1b, 5	...	220
$(C_2H_5)_3SnC\equiv CC(CH_3){=}CH_2$	...	97–97.5 (10)	1.5040	1.2043	...	...	134
	...	97–97.5 (10)	1.5040	1.2043	4	73	249, 251

TABLE XXI (*Continued*)

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(C_2H_5)_3SnC\equiv CCH=CHCH_3$	...	107–108 (10)	1.5102	1.1924	...	...	134
	...	104–105 (10)	1.5112	1.2183	4	...	249
$(C_3H_7)_3SnC\equiv CCH=CH_2$	...	100–101 (3)	1.4938	1.1391	5	...	205
$(C_4H_9)_3SnC\equiv CCH=CH_2$	...	135–136 (3.5)	1.4955	1.0928	2, 5	...	205
	...	110 (1.5)	1.4520	1.1004	...	87.5	208
$(C_6H_5)_3SnC\equiv CCH=CH_2$	58	...	...	...	...	58	102
	58–59	...	...	...	2, 4		103
	58	...	...	...	...	81	208
$(C_6H_5)_3SnC\equiv CC(CH_3)=CH_2$	106	...	...	...	...	66	102
	64	...	...	...	...	77	103
F. $R_3SnC\equiv CSnR_3$							
$(CH_3)_3SnC\equiv CSn(CH_3)_3$	58	102 (23)	...	...	...	...	220
	...	63 (1)	1.5556	1.5202	4, 5, 6a	...	255
	57.5–59	97–98 (16)	...	...	...	78	104
$(C_2H_5)_3SnC\equiv CSn(C_2H_5)_3$	...	136–137 (5)	1.5089	...	...	52.5 (20)	104, 205
	...	123 (0.05)	...	...	1a, 2, 6a	...	51
$(C_3H_7)_3SnC\equiv CSn(C_3H_7)_3$	...	136–137 (0.1)	1.5005	...	...	94	104
	...	178–179 (3)	1.5040	1.2461	5, 6a	...	205
	...	188–189 (6)	...	...	...	92	220
$(C_4H_9)_3SnC\equiv CSn(C_4H_9)_3$	...	158–159 (0.08)	1.4935	...	...	92	104
	...	204 (3)	1.4888	1.401	5, 6a	...	205
$(C_6H_5)_3SnC\equiv CSn(C_6H_5)_3$	140–142.5	...	...	...	...	37.5	104
	153	...	...	...	1a, 6a	...	8
	152	...	...	...	...	80	103
$(p\text{-}ClC_6H_4)_3SnC\equiv CSn(C_6H_4Cl\text{-}p)_3$	191	...	...	...	1a, 2	...	51
$[1,2(CH_3)_2C_6H_4]_3SnC\equiv CSn[C_6H_3\text{-}1,2\text{-}(CH_3)_2]_3$	143	...	...	...	1a, 2	...	51
$[1,4(CH_3)_2C_6H_4]_3SnC\equiv CSn[C_6H_3\text{-}1,4\text{-}(CH_3)_2]_3$	149	...	...	...	1a, 2	...	51
$(C_6H_5CH_2)_3SnC\equiv CSn(CH_2C_6H_5)_3$	94	...	...	...	1a, 2	...	51
$(C_2H_5)_3SnC\equiv CSn(CH_3)_2$	...	59 (1.5)	1.4710	1.1162	5	...	220
$(C_2H_5)_3SnC\equiv CSi(CH_3)_3$	...	107 (9)	1.4805	1.1456	5	...	220
G. $R_3SnC\equiv CXC\equiv CSnR_3$							
$(C_6H_5)_3SnC\equiv C(CH_2)_3C\equiv CSn(C_6H_5)_3$	105	...	...	...	2	40	103
$(C_6H_5)_3SnC\equiv (CH_2)_4C\equiv Sn(C_6H_5)_3$	148	...	...	...	2	50	103
$(C_6H_5)_3SnC\equiv CC_6H_4C\equiv CSn(C_6H_5)_3$	205	...	...	...	2	15	103
$(C_6H_5)_3SnC\equiv C(C_{14}H_8)C\equiv CSn(C_6H_5)_3$[h]	225	...	...	...	2	57	103
H. $R_3SnC\equiv CC\equiv CR$							
$(C_3H_7)_3SnC\equiv CC\equiv CH$	...	103 (1)	1.5110	1.1343	5	...	220
$(C_6H_5)_3SnC\equiv CC\equiv CH$	99 dec	...	...	...	1a	30	103, 108
$(C_2H_5)_3SnC\equiv CC\equiv CC_2H_5$	...	100–101 (1)	1.5293	1.2127	5	...	210
$(C_6H_5)_3SnC\equiv CC\equiv CCH_3$	...	Oil	...	...	1a	40	103, 108
$(C_6H_5)_3SnC\equiv CC\equiv CC_6H_5$	68–88	...	...	...	1a	60	103, 108
$(C_2H_5)_3SnC\equiv CC\equiv CH$	...	60 (1)	1.5262	1.2626	5	50	220
	...	67–68 (2)	1.5273	1.2891	...	...	210
I. $R_3Sn(C\equiv C)_2SnR_3$							
$(CH_3)_3SnC\equiv CC\equiv CSn(CH_3)_3$	140	...	...	...	1a	76.5	64
$(C_2H_5)_3SnC\equiv CC\equiv CSn(C_2H_5)_3$	...	156 (0.5)	1.5483	1.3646	5	46.4	220
$(C_4H_9)_3SnCC\equiv CSn(C_4H_9)_3$	...	Oil	1.5116[i]	...	1a	71	64
$(C_6H_5)_3SnC\equiv CC\equiv CSn(C_6H_5)_3$	245 dec	...	...	...	...	40	108, 108 59
$(p\text{-}ClC_6H_4)_3SnC\equiv CC\equiv CSn(C_6H_4Cl\text{-}p)_3$	204	...	...	...	1a	94	65
$(p\text{-}CH_3C_6H_4)_3SnC\equiv CC\equiv CSn(C_6H_4CH_3\text{-}p)_3$	208	...	...	...	1a	94	65
$(C_6H_{11})_3SnC\equiv CC\equiv CSn(C_6H_{11})_3$	210	...	...	...	1a	84	65
$(C_6H_{13})_3SnC\equiv CC\equiv CSn(C_6H_{13}\text{-}n)_3$	...	Oil	1.4946	...	1a	76	65
$(n\text{-}C_8H_{17})_3SnC\equiv CC\equiv CSn(C_8H_{17}\text{-}n)_3$	...	Oil	1.4905	...	1a	87	65
$(C_6H_5)_3SnC\equiv CC\equiv CC\equiv CSn(C_6H_5)_3$	170 dec	...	...	...	2	30	108

[a] Temperature 18°. [b] 1-Cyclopentenyl. [c] 1-Cyclohexenyl. [d] Synthesized from other acetylene compounds. [e] Δ^2-Pyrazoline. [f] 9-Anthranyl. [g] Acetal derivative (see footnote *b*, Table XV). [h] 9,10-Substituted anthracene. [i] Temperature 22°.

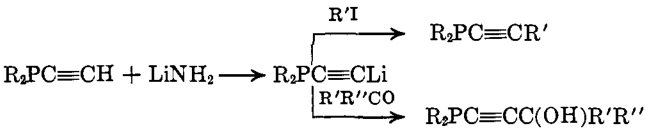
TABLE XXII
ALKYNYLLEAD COMPOUNDS

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
		A. $Pb(C\equiv CR)_4$					
$Pb(C\equiv CC_6H_4Br)_4$	155	...	...	...	1b	22	67
$Pb(C\equiv CC_6H_{11})_4$	94	...	...	...	1b	22.5	66
		B. $R_3PbC\equiv CR$					
$(CH_3)_3PbC\equiv CCH_3$		65.5 (16)			1a	27	7
$(CH_3)_3PbC\equiv CC_2H_5$		54 (4)			1a	11	7
$(C_2H_5)_3PbC\equiv CH$	...	110 (2.5)	...	...	1a, 1b	30	108, 109
$(C_2H_5)_3PbC\equiv CCH_3$	...	81 (1.5)	...	...	1a, 1b	40	108, 109
$(C_2H_5)_3PbC\equiv CC_2H_5$	...	105 (3)	...	...	1a, 1b	64	108, 109
$(C_2H_5)_3PbC\equiv CC_5H_7{}^a$	...	95 (1.5)	...	...	1a, 1b	30	108
$(C_2H_5)_3PbC\equiv CC_6H_5$	...	66 (1)	...	...	1a, 1b	42	108, 109
$(C_2H_5)_3PbC\equiv CCH\equiv CH_2$	...	114–114.5 (6)	1.5602	1.5564	4	...	249
$(C_2H_5)_3PbC\equiv CC(CH_3){=}CH_2$	...	93–94 (3)	1.5849	1.5462	4	...	249
$(C_6H_5)_3PbC\equiv CH$	...	Oil	...	...	1a, 1b	50	109
		B. $R_3PbC\equiv CR$					
$(C_6H_5)_3PbC\equiv CBr$	95	...	...	...	1a	28	109
$(C_6H_5)_3PbC\equiv CCH_3$	65	Oil	...	...	1a, b	50	108, 109
$(C_6H_5)_3PbC\equiv CC_2H_5$	64	...	...	...	1a, b	53	108, 109
$(C_6H_5)_3PbC\equiv C_6H_5$	56	...	...	...	1a, b	52	108, 109
$(C_6H_5)_3PbC\equiv CC_5H_7{}^a$	50	...	...	...	1a, b	41	108, 109
$(C_6H_5)_3PbC\equiv CC_6H_9{}^b$	84	...	...	...	1a, b	53	108, 109
		C. $R_3PbC\equiv CPbR_3$					
$(C_2H_5)_3PbC\equiv CPb(C_2H_5)_3$	...	135–140	...	...	1a	...	8, 109
	...	(0.05) dec	...	...	...	...	
$(C_6H_5)_3PbC\equiv CPb(C_6H_5)_3$	138.5	...	...	...	1a	...	8, 109
	136	...	...	...	...	...	
$(p\text{-}CH_3C_6H_4)_3PbC\equiv CPb(C_6H_4CH_3\text{-}p)_3$	130	Moisture sensitive		...	1a	...	55
$(o\text{-}CH_3C_6H_4)_3PbC\equiv CPb(C_6H_4CH_3\text{-}o)_3$	121	Moisture sensitive		...	1a	...	55
$(C_6H_5CH_2CH_2)_3PbC\equiv CPb(CH_2CH_2C_6H_5)_3$	62	Light and moisture sensitive			1a	...	55
$(C_6H_{11})_3PbC\equiv CPb(C_6H_{11})_3$	136	Light and moisture sensitive			1a	...	55
		D. $R_3PbC\equiv CC\equiv CR$					
$(C_6H_{11})_3PbC\equiv CC\equiv CH$	...	115 (4) dec	...	...	1a, b	90	63, 108
$(C_6H_{11})_3PbC\equiv CC\equiv CC_2H_5$	68	175 (760) dec	...	...	1a, b	80	108
$(C_6H_{11})_3PbC\equiv CC\equiv CC_3H_7\text{-}n$	...	140 (4) dec	...	...	1a, b	66	108
$(C_6H_5)_3PbC\equiv CC\equiv CH$	93 (dec)	...	...	...	1a, b	30	109
$(C_6H_{11})_3PbC\equiv CC\equiv CC_4H_9\text{-}n$	...	150 (4) dec	...	...	1a, b	54	108
$(C_6H_5)_3PbC\equiv CC\equiv CCH_3$	55	...	...	...	1a, b	42	108, 109
$(C_6H_5)_3PbC\equiv CC\equiv CC_6H_5$	81	...	...	...	1a, b	55	108, 109
		E. $R_3Pb(C\equiv C)_nPbR_3$					
$(C_2H_5)_3PbC\equiv CC\equiv CPb(C_2H_5)_3$	80	...	...	...	1a	83	63
$(C_6H_5)_3PbC\equiv CC\equiv CPb(C_6H_5)_3$	187	...	...	...	1a, b	40	59, 108, 109
$(C_6H_{11})_3PbC\equiv CC\equiv CPb(C_6H_{11})_3$	138	...	...	...	1a	13	63
$(C_2H_5)_3PbC\equiv CC\equiv CC\equiv CPb(C_2H_5)_3$	110 dec	...	...	...	1a	70	63
$(C_6H_5)_3PbC\equiv CC\equiv CC\equiv CPb(C_6H_5)_3$	150 dec	...	...	...	1a	65	63
$(C_6H_{11})_3PbC\equiv CC\equiv CC\equiv CPb(C_6H_{11})_3$	148 dec	...	...	...	1a	52	63

[a] Cyclopentenyl. [b] Cyclohexenyl.

1. *Reactions of Dialkylethynylphosphine, $R_2PC\equiv CH$*

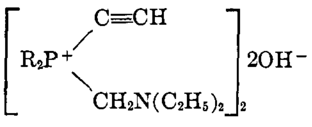
Dibutylethynylphosphine interacts with lithium amide in liquid ammonia to give the expected corresponding lithium compound in high yield (236). This compound can be reacted with alkyl halides and ketones



$$R_2PC\equiv CH + LiNH_2 \longrightarrow R_2PC\equiv CLi \begin{cases} \xrightarrow{R'I} R_2PC\equiv CR' \\ \xrightarrow{R'R''CO} R_2PC\equiv CC(OH)R'R'' \end{cases}$$

An attempt to achieve a Mannich reaction with dibutylethynylphosphine was not successful, acetylene and N,N-diethylaminomethylphosphine oxide being the only reaction products detected. It has been suggested that the reaction involves the intermediate formation of a quaternary phosphonium hydroxide

$$R_2PC\equiv CH + CH_2O + HN(C_2H_5)_2 \longrightarrow$$



$$\left[R_2P^+\begin{matrix} C\equiv CH \\ CH_2N(C_2H_5)_2 \end{matrix}\right]_2 2OH^-$$

The free-radical addition of ethanethiol to dialkylethynylphosphine in the presence of azobisisobutyronitrile or ultraviolet irradiation proceeds smoothly

TABLE XXIII
ALKYNYLPHOSPHORUS COMPOUNDS

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
A. $P(C\equiv CR)_3$							
$P(C\equiv CH)_3$	36–37	52 (30)	...	...	2	57.4	237
$P(C\equiv CC_6H_5)_3$	92, 91	...	...	...	1b, 2	90	28, 56
$P(C\equiv CC_6H_4Cl)_3$	192 dec	...	...	...	2	...	61
$P(C\equiv CC_6H_4CH_3)_3$	125	...	...	...	2	...	61
$P(C\equiv CC_{14}H_9)_3{}^a$	250	...	...	...	2	89	28
B. $RP(C\equiv CR)_2$							
$C_6H_5P(C\equiv CC_{14}H_9)_2{}^a$	193	...	...	...	2	90	28
C. $R_2PC\equiv CR$							
$(C_2H_5)_2PC\equiv CH$	...	128 (760)	...	...	2	48	25
	...	66–67 (77)	1.4808	...	...	49	236
$(n\text{-}C_3H_7)_2PC\equiv CH$	...	55 (11)	1.4770	...	2	60	236
$(n\text{-}C_4H_9)_2PC\equiv CH$	...	85 (10)	1.4765	...	2	70	236
$(n\text{-}C_5H_{11})_2PC\equiv CH$	...	65 (0.35)	1.4759	...	2	72.5	236
$(C_6H_5)_2PC\equiv CH$	35	...	...	...	2	90	25
$(C_2H_5)_2PC\equiv CCH_3$	...	165 (760)	...	...	2	50	25
$(C_2H_5)_2PC\equiv CC_6H_5$	...	105 (0.8)	...	...	2	52	25
$(C_2H_5)_2PC\equiv CC_6H_9{}^b$	...	120 (2)	...	...	2	50	25
$(n\text{-}C_4H_9)_2PC\equiv CCH_3$	...	66–67 (1)	1.4867	...	2	81	236
$(n\text{-}C_4H_9)_2PC\equiv CC_2H_5$	...	58 (0.25)	1.4848	...	2	84	236
$(n\text{-}C_4H_9)_2PC\equiv CC_6H_5$	...	105–108 (0.001)	1.5570	...	2	88	236
$(n\text{-}C_4H_9)_2PC\equiv CSC_2H_5$	...	78 (0.001)	1.5265	...	2	81	236
$(n\text{-}C_4H_9)_2PC\equiv CC(CH_3)_2OH$	...	91 (0.03)	1.4871	...	2	58	236
$(n\text{-}C_4H_9)_2PC\equiv CC_6H_{10}OH^c$	25	105 (0.001)	1.5090	...	2	70	236
$(n\text{-}C_4H_9)_2PC\equiv CCH=CH_2$	...	92 (3)	1.5110	0.8602	2	...	106
$(C_6H_5)_2PC\equiv CCH_3$	33	143 (0.1)	...	...	2	56	25
$(C_6H_5)_2PC\equiv CC_6H_5$	43, 44	...	...	...	2, 4	93	25, 28, 77
$(C_6H_5)_2PC\equiv CCH_2C_{14}H_9{}^a$	178	...	...	...	2	74	25
$(C_6H_5)_2PC\equiv CC(CH_3)_2OH$	76	...	...	...	2	79	25, 28
$(C_6H_5)_2PC\equiv CC_5H_7{}^d$	42	...	...	...	2	72	25
$(C_6H_5)_2PC\equiv CC_6H_9{}^b$	60	...	...	...	2	70	25
$(C_6H_5)_2PC\equiv CC_7H_{11}{}^e$	...	...	...	...	2	...	25
$(C_6H_5)_2PC\equiv CCH=C(C_6H_5)_2$	...	...	...	...	2	...	25
$(C_6H_5)_2PC\equiv CC(C_6H_5)_2OH$	143	...	...	...	...	95	28
$(C_6H_5)_2PC\equiv CC_{13}H_8OH^f$	133	...	...	...	*g*	85	28
$(C_6H_5)_2PC\equiv CR^h$	202	...	...	...	*g*	90	28
$(C_6H_{11})_2PC\equiv CC_6H_5$	74	...	...	...	4	35	77
D. $(RC\equiv C)_3PX$							
$(C_6H_5C\equiv C)_3PO$	126	...	...	...	2	77	28
$(C_6H_5C\equiv C)_3PS$	138.4–138.8	...	...	...	*g*	50	17
$(CH_3C_6H_4C\equiv C)_3PO$	177	...	...	...	...	...	61
$(CH_3H_6H_4C\equiv C)_3PS$	180 dec	...	...	...	*g*	...	61
$(CH_3C_6H_4C\equiv C)_3PSe$	162 dec	...	...	...	*g*	...	61
$(CH_3C\equiv C)_3PS$	198.2–198.8	...	...	...	2	35	17
E. $R'(RC\equiv C)_2PX$							
$(CH_3C\equiv C)_2P(CH_3)S$	38.2–38.8	...	...	...	2	28	17
$(C_6H_5C\equiv C)_2P(CH_3)S$	91.3–91.6	...	...	...	2	60	17
$(CH_3C\equiv C)_2P(C_6H_5)S$	67.8–68.4	...	...	...	2	30	17
$(C_6H_5C\equiv C)_2P(C_6H_5)S$	129.6–130	...	...	...	2	85	17
F. $R'_2(RC\equiv C)PX$							
$CH_3C\equiv CP(CH_3)_2S$	77.5–78.2	...	...	...	2	62	18
$C_6H_5C\equiv CP(CH_3)_2S$	92.4–93.2	...	...	...	2	86	18
$CH_2\equiv CHC\equiv CP(CH_3)_2S$	42–43	...	...	...	2	63	18
$C_6H_5C\equiv CP(C_2H_5)_2O$	...	160 (0.6)	...	...	*g*	30	25
$C_6H_9C\equiv CP(C_2H_5)_2O^b$	...	140 (0.3)	...	...	*g*	30	25
$HC\equiv CP(C_6H_5)_2O$	68	...	...	...	*g*	92	25
$CH_3C\equiv CP(C_6H_5)_2O$	94	...	...	...	*g*	51	25
$CH_3C\equiv CP(C_6H_5)_2S$	88	...	...	...	*g*	68	25
$C_6H_5C\equiv CP(C_6H_5)_2O$	102	...	...	...	*g*	87	25
$C_6H_5C\equiv CP(C_6H_5)_2S$	113, 111.5	...	...	...	*g*	76	77
$HO(CH_3)_2CC\equiv CP(C_6H_5)_2O$	162	...	...	...	*g*	78	25
$HO(CH_3)_2CC\equiv CP(C_6H_5)_2S$	127	...	...	...	*g*	73	26

TABLE XXIII (*Continued*)

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$C_5H_7C\equiv CP(C_6H_5)_2O$[d]	130	...	...	...	*g*	74	25
$C_5H_7C\equiv CP(C_6H_5)_2S$[d]	93	...	...	...	*g*	61	25
$C_6H_9C\equiv CP(C_6H_5)_2O$[b]	120	...	...	...	*g*	78	25
$C_6H_9C\equiv CP(C_6H_5)_2S$[b]	120	...	...	...	*g*	69	25
$C_7H_7C\equiv CP(C_6H_5)_2O$[e]	114	...	...	...	*g*	40	25
$(C_6H_5)_2C=CHC\equiv CP(C_6H_5)_2$	136	...	...	...	*g*	32	25
$C_6H_5C\equiv CP(C_6H_{11})_2S$	156	...	...	...	*g*	...	77
$CH_3C\equiv CP(Cl_2)O$	...	56–57 (1.5)	1.4912	1.3953	*g*	92.5	107
$CH_2=CHC\equiv CP(Cl_2)O$	...	61–65 (2.5)	1.5150	1.3784	*g*	28	107
$C_6H_5C\equiv CP(Cl_2)O$	...	121–124 (0.5)	1.5938	1.3650	*g*	36	107
G. $[R(C\equiv C)_n]_3P(X)$							
$(CH_3C\equiv CC\equiv C)_3P$	117	...	...	...	*i*	73	62
$(CH_3C\equiv CC\equiv C)_3PO$	85 dec	...	...	...	*g*	56	62
$(C_2H_5C\equiv CC\equiv C)_3P$	71	...	...	...	*i*	62	62
$(C_6H_5C\equiv CC\equiv C)_3P$	127 dec	...	...	...	*i*	28	62
$CH_3C\equiv CC\equiv CP(C_2H_5)_2$	...	85 (1)	...	...	*g*	40	25
$HC\equiv CC\equiv CP(C_6H_5)_2$	52	...	...	...	*g*	35	25
$CH_3C\equiv CC\equiv CP(C_6H_5)_2$	61	...	...	...	*g*	74	25
$CH_3C\equiv CC\equiv CP(C_6H_5)_2O$	84	...	...	...	*g*	71	25
$CH_3C\equiv CC\equiv CP(C_6H_5)_2S$	71	...	...	...	*g*	58	25
n-$C_3H_7C\equiv CC\equiv CP(C_6H_5)_2$	44	...	...	...	*g*	78	25
n-$C_3H_7C\equiv CC\equiv CP(C_6H_5)_2O$	64	...	...	...	*g*	67	25
$C_6H_5C\equiv CC\equiv CP(C_6H_5)_2$	75	...	...	...	2	77	25
$C_6H_5C\equiv CC\equiv CP(C_6H_5)_2O$	131	...	...	...	*g*	74	25
$C_6H_5C\equiv CC\equiv CP(C_6H_5)_2S$	89	...	...	...	*g*	63	25
$CH_3C\equiv CC\equiv CC\equiv CP(C_6H_5)_2$	131	...	...	...	2	65	25
H. $R_2PC\equiv CPR_2$							
$(n\text{-}C_4H_9)_2PC\equiv CP(C_4H_9\text{-}n)_2$	33	...	...	...	2	...	236
$(C_6H_5)_2PC\equiv CP(C_6H_5)_2$	86	193 (3×10^{-6})	...	...	1a, 2	...	48, 49
I. $R_2P(X)C\equiv CP(X)R_2$							
$(C_6H_5)_2P(O)C\equiv CP(O)(C_6H_5)_2$	164–163	...	...	...	*g*	87	48, 49
$(C_6H_5)_2P(S)C\equiv CP(S)(C_6H_5)_2$	186	...	...	...	*g*	75	
	157.5	...	...	...	*g*	...	48, 49
J. $R_2PC\equiv CPR_2\cdot R'X$							
$[(C_6H_5)_2(CH_3)PC\equiv CP(C_6H_5)_2]I$	156	...	...	...	*g*	90	49
$[(C_6H_5)_2(C_2H_5)PC\equiv CP(C_6H_5)_2]I$	128	...	...	...	*g*	84	49
K. $RP(O)(C\equiv CR')_2$							
$HO(O)P(C\equiv CC_6H_5)_2$	146–147	...	...	...	*g*	68	37
$Cl(O)P(C\equiv CC_6H_5)_2$	Undistillable greenish oil	...	...	...	...	95	37
$C_6H_5O(O)P(C\equiv CC_6H_5)_2$	83–84	...	...	...	*g*	50	37
p-$ClC_6H_4O(P)(C\equiv CC_6H_5)_2$	96–97	...	...	...	*g*	68	37
m-$NO_2C_6H_4O(O)P(C\equiv CC_6H_5)_2$	105–106.5	...	...	...	*g*	98	37
p-$NO_2C_6H_4O(O)P(C\equiv CC_6H_5)_2$	103–104	...	...	...	*g*	55	37
$C_6H_5NH(O)P(C\equiv CC_6H_5)_2$	179–179.5	...	...	...	*g*	98	37
p-$CH_3C_6H_4NH(O)P(C\equiv CC_6H_5)_2$	176–177	...	...	...	*g*	76	37
$(2,4\text{-}Cl_2C_6H_3NH)(O)P(C\equiv CC_6H_5)_2$	121.5–122	...	...	...	*g*	50	37
p-$ClC_6H_4NH(O)P(C\equiv C_6H_5)_2$	140–142	...	...	...	*g*	94	37
p-$BrC_6H_4NH(O)P(C\equiv CC_6H_5)_2$	143–145	...	...	...	*g*	97	37
p-$CH_3OC_6H_4NH(O)P(C\equiv CC_6H_5)_2$	132–133	...	...	...	*g*	98	37
L. $R_2P(O)C\equiv CR'$							
$(HO)_2(O)PC\equiv CC_6H_5$	142	...	...	...	6f	...	11
$(HO)_2(O)PC\equiv CC_6H_4Cl$-$o$	142	...	...	...	6f	...	11
$(CH_3O)_2(O)PC\equiv C(CH_2)_3OC_6H_5$	...	206 (4)	1.5212	1.1504	6f	83	4
$(C_2H_5O)_2(O)PC\equiv CCH_3$	...	91–91.5 (3)	1.4472	1.0717	...	92.5	75
	...	95 (0.5)	1.4450[k]	...	4	37	227
	...	115–116 (4)	1.4460[l]	1.0734	...	68.5	148
$(C_2H_5O)_2(O)PC\equiv CC_4H_9$-$n$	...	115 (0.6)	1.4478[k]	...	4	50	227
$(C_2H_5O_2)(O)PC\equiv CC_5H_{11}$-$n$	...	125 (0.4)	1.4481[m]	...	4	73	227
$(C_2H_5O)_2(O)PC\equiv CC_6H_{13}$-$n$	...	128 (0.4)	1.4470[m]	...	4	50	227
$(C_2H_5O)_2(O)PC\equiv CC_6H_5$	...	139 (0.2)	1.5310	...	...	45	227
	...	154.5 (2)	...	...	4	67	72

TABLE XXIII (*Continued*)

Compound	Mp, °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(C_2H_5O)_2(O)PC{\equiv}CC(CH_3)_2OH$	...	133 (0.4)	1.4500[n]	...	4	68	227
$(C_2H_5O)_2(O)PC{\equiv}C(CH_2)_3OC_6H_5$	...	190 (3)	1.5050	1.1091	6f	75	4
$(CH_3O)_2(O)PC{\equiv}CCH{=}CH_2$	...	110–112 (3.5)	1.4740	1.1358	*j*	21.5	107
$(C_2H_5O)_2(O)PC{\equiv}CCH{=}CH_2$	...	107–108 (2.5)	1.4696	1.0630	...	48	72, 74
$(C_2H_5O)_2(O)PC{\equiv}CCH{=}CHCH_3$	...	112–115 (2)	1.4790	1.0610	*j*	...	74
$(C_2H_5O)_2(O)PC{\equiv}CC(CH_3){=}CH_2$	...	110–111 (3)	1.4696	1.0549	...	...	74
	...	90 (0.4)	1.4630[k]	...	4	...	227
$(C_3H_7O)_2(O)PC{\equiv}CCH_3$	...	127–128 (4)	1.4478	1.0279	*i*	60.2	148
$(n\text{-}C_4H_9O)_2(O)PC{\equiv}CCH_3$	...	152–153 (6)	1.4498	1.0029	*i*	67.3	148
$(i\text{-}C_4H_9O)_2(O)PC{\equiv}CC_6H_5$	...	159–161 (1)	1.5090	1.0423	6f	...	3
$(C_6H_5O)_2(O)PC{\equiv}CC_6H_5$	...	155 (1)	1.5312	1.11500	6f	...	3
$(C_2H_5O)_2(O)PC{\equiv}CN(C_2H_5)_2$		145–147 (1)	1.4680	1.0538	*g*	44	76
M. $R_2P(O)C{\equiv}CC{\equiv}CR'$							
$(C_2H_5O_2)(O)PC{\equiv}CC{\equiv}CCH_3$	...	134.5–136.5 (1.5)	1.4930	1.0753	*j*	...	73
$(C_2H_5O)_2(O)PC{\equiv}CC{\equiv}CC_2H_5$	...	130–131 (0.5)	1.4897	1.0215	*j*	...	73

[a] 9-Anthryl. [b] Cyclohexenyl-1. [c] *p*-Hydroxycyclohexyl. [d] Cyclopentenyl-1. [e] Cycloheptenyl-1. [f] 1-Hydroxyfluorenyl-1. [g] Synthesized from other acetylenic compounds. [h] 1-Hydroxyanthrafuschone (Fr). [i] Redistribution reaction, $3R_2Hg + 2PI_3 \rightarrow 3HgI_2 + 2R_3P$. [j] Arbuzov reaction. [k] 24°. [l] 26°. [m] 22°. [n] 25°.

$$R_2PC{\equiv}CH + 3C_2H_5SH \longrightarrow R_2PCH{=}CSC_2H_5 + C_2H_5SC_2H_5 + H_2S$$

The ionic addition of sodium ethanethiolate, however, does not proceed under the conditions used. Bis(dibutylphosphinyl)acetylene is formed in high yield. Similar to the cleavage of bis(triphenylsilyl)acetylene (46), bisdibutylphosphinylacetylene reacts with phenyllithium to form dibutylethynylphosphine (236)

$$R_2PC{\equiv}CPR_2 + C_6H_5Li \xrightarrow[H_2O]{\text{ether}} R_2PC{\equiv}CH + R_2PC_6H_5$$

Both products are formed in high yields.

2. Reactions of Alkynylphosphines

Bisdiphenylethynylphosphine has been thoroughly investigated (49). In addition it is the earliest reported alkynylphosphine in the literature. The compound has good thermal and hydrolytic stability and is not sensitive toward oxygen. Silver ions do not cleave the phosphorus–carbon bond. The dioxide is formed through oxidation with hydrogen peroxide in high yield and the reaction with sulfur gives the corresponding sulfide

$$(C_6H_5)_2P(O)C{\equiv}CP(O)(C_6H_5)_2 \quad (C_6H_5)_2P(S)C{\equiv}CP(S)(C_6H_5)_2$$

A large number of oxides and sulfides of alkynylphosphorus compounds have been prepared (25, 61) and a selenium derivative is also known, $(H_3CC_6H_4C{\equiv}C)_3PSe$ (61).

The oxides and sulfides can also be prepared from acetylenic Grignards and the corresponding phosphorus halogen oxides or sulfides (17, 18, 28). Contrary to bisdiphenylphosphinylacetylene, its analogous oxide and sulfide cleave readily with boiling alcoholic potassium hydroxide. Phosphonium salts are formed with methyl and ethyl iodide.

C. ALKYNYLPHOSPHONIC ACIDS AND THEIR ESTERS

Alkynylphosphonic acids and dialkynylphosphinic acids can be synthesized by dehydrohalogenation of halostyrylphosphonic acids

$$C_6H_5(Cl)C{=}C(H)P(O)(OH)_2 \xrightarrow{KOH} C_6H_5C{\equiv}CP(O)(OH)_2 \quad (11)$$

$$[C_6H_5(Cl){=}C(H)]_2P(O)OH \xrightarrow{KOH} (C_6H_5C{\equiv}C)_2P(O)OH \quad (37)$$

The corresponding esters undergo the same reaction (3). These compounds have been transformed into the chlorides with phosphorus pentachloride (107)

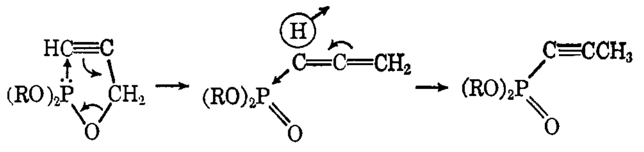
$$(C_6H_5C{\equiv}C)_2P(O)OH \xrightarrow{PCl_5} (C_6H_5C{\equiv}C)_2P(O)Cl$$

$$CH_3C{\equiv}CP(O)(OC_2H_5)_2 \xrightarrow{PCl_5} CH_3C{\equiv}CP(O)Cl_2$$

Phosphonic acid esters can be synthesized from trialkylphosphites and alkyl halides. This reaction, known as the Arbuzov rearrangement, takes place with a number of alkynyl bromides (72, 73) and alkyldiacetylene bromides (74)

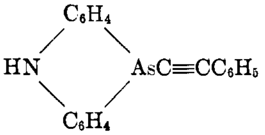
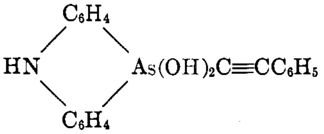
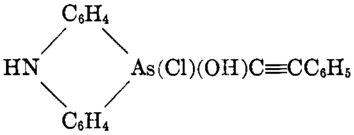
$$R'C{\equiv}CBr + (RO)_3P \longrightarrow R'C{\equiv}CP(O)(OR)_2 + RBr$$

Another method is the nucleophilic substitution of alkynyl bromides by sodium diethylphosphite (227). Some nucleophilic addition reactions of alkynylphosphonic acid esters are reported (148). Dialkyl(2-propynyl)phosphites undergo a thermal rearrangement in the presence of organic base to form the 1-propynylphosphonic acid ester (149). It is assumed that the



I II III

TABLE XXIV
ALKYNYLARSENIC COMPOUNDS

Compound	Mp °C	Bp, °C (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$As(C\equiv CH)_3$	49–50	...	...	...	2	62.6	237
$As(C\equiv CCH_3)_3$	131	...	...	...	2	92	9
$As(C\equiv CC_6H_5)_3$	127	...	...	...	1b, 2	...	56
$C_6H_5As(C\equiv CCH_3)_2$	...	75 (0.01)	...	...	2	85	9
$C_6H_5As(C\equiv CC_6H_5)_2$	63	...	...	...	2	63	9
$(C_6H_5)_2AsC\equiv CH$	23	140 (1.5)	...	...	2	85	9
$(C_6H_5)_2AsC\equiv CCH_3$	...	128 (1)	...	...	2	86	9
$(C_6H_5)_2AsC\equiv CC_2H_5$	...	110 (0.01)	...	...	2	92	9
$(C_6H_5)_2AsC\equiv CC_6H_5$	43	168 (3)	...	...	1b, 2	...	57
$(C_6H_5)_2AsC\equiv CC_6H_9$	42	...	...	...	2	70	9
$(C_6H_5)_2AsC\equiv CCOOH$	130	...	...	...	[a]	58	9
$(C_6H_5)_2AsC\equiv C\underbrace{C(OH)(CH_2)_4CH_2}$	57	...	...	...	[a]	87	9
$(C_6H_5)_2AsC\equiv CC(C_6H_5)_2OH$	136	...	...	...	[a]	87	9
$(\alpha\text{-}C_{10}H_7)_2AsC\equiv CH$	123	...	...	...	1b, 2	...	57
$(\alpha\text{-}C_{10}H_7)_2AsC\equiv CC_6H_5$	142	...	...	...	1b, 2	...	57
	172	...	...	...	1b	...	156
$(C_6H_5)_2As(O)C\equiv CCH_3$	105	...	...	...	[a]	95	9
$(C_6H_5)_2As(OH)_2C\equiv CCH_3$	68	...	...	...	[a]	95	9
$(C_6H_5)_2As(O)C\equiv CC_2H_5$	130	...	...	...	[a]	95	9
$(C_6H_5)_2As(OH)_2C\equiv CC_2H_5$	80	...	...	...	[a]	95	9
$(C_6H_5)_2As(O)C\equiv C\underbrace{C(OH)(CH_2)_4CH_2}$	205	...	...	...	[a]	90	9
$(C_6H_5)_2As(O)C\equiv CC(C_6H_5)_2OH$	260 dec	...	...	...	[a]	90	9
	150 dec	...	...	...	1b	...	156
	148	...	...	...	1b	...	156
$(C_2H_5)_2AsC\equiv CAs(C_2H_5)_2$	...	139 (8)	...	...	2	72	50
$(C_6H_{11})_2AsC\equiv CAs(C_6H_{11})_2$	72	...	...	...	2	70	50
$(C_6H_5)_2AsC\equiv CAs(C_6H_5)_2$	105	...	...	...	1a, 2	74	48,50
$(\alpha\text{-}C_{10}H_7)_2AsC\equiv CAs(C_{10}H_7\text{-}\alpha)_2$	232	...	...	...	1a, 2	61	50
$(\alpha\text{-}C_{10}H_7)_2As(O)C\equiv C(O)As(C_{10}H_7\text{-}\alpha)_2$	218.5 dec	...	...	...	[a]	...	50
$(C_2H_5)_2AsC\equiv CC\equiv CCH_3$	...	70 (0.5)	...	...	2	83	9
$(C_6H_5)_2AsC\equiv CC\equiv CH$	55	...	...	...	1a, 2	48	9
$(C_6H_5)_2AsC\equiv CC\equiv CCH_3$	60	...	...	...	2	76	9
$(C_6H_5)_2AsC\equiv CC\equiv CC_3H_7$	40	...	...	...	2	75	9
$(C_6H_5)_2AsC\equiv CC\equiv CC_6H_5$	63	...	...	...	2	55	9
$(C_6H_5)_2AsC\equiv CC\equiv CC\equiv CCH_3$	125	...	...	...	2	60	9
$(C_6H_5)_2AsC\equiv CC\equiv CAs(C_6H_5)_2$	114 dec	...	...	...	1a	40	9, 65
$(\alpha\text{-}C_{10}H_7)_2AsC\equiv CC\equiv CAs(C_{10}H_7\text{-}\alpha)_2$	218 dec	...	...	...	...	50	65
$[(C_6H_5)_2As^+(CH_3)C\equiv CH]TsO^-$	159	...	...	...	[a]	10	9
$[(C_6H_5)_2As^+(CH_3)C\equiv CCH_3]TsO^-$	170	...	...	...	[a]	30	9
$[(C_6H_5)_2As^+(CH_3)C\equiv CC(C_6H_5)_2OH]I^-$	260 dec	...	...	...	[a]	10	9
$[(C_2H_5)_2As^+(CH_3)C\equiv CC\equiv CCH_3]I^-$	137 dec	...	...	...	[a]	92	9
$[(C_2H_5)_3As^+C\equiv CC\equiv CCH_3]Br^-$	160	...	...	...	[a]	98	9
$[(C_2H_5)_3As^+C\equiv CC\equiv CC_6H_5]Br^-$	170–180 dec	...	...	...	[a]	95	9
$[(C_2H_5)_2As^+(CH_3)C\equiv CAs(C_2H_5)_2)]^-$	68	...	...	...	[a]	...	50
$[(C_6H_{11})_2As^+(CH_3)C\equiv CAs(C_6H_{11})_2]I^-$	133	...	...	...	[a]	...	50

[a] Synthesized from other acetylene compounds.

TABLE XXV
ALKYNYLANTIMONY COMPOUNDS

Compound	Mp, °C	Bp (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$Sb(C\equiv CH)_3$	71–72	...	...	...	2	63.1	237
$Sb(C\equiv CC_6H_5)_3$	159 dec	...	...	...	1b, 2	...	56
$p\text{-}CH_3C_6H_4Sb(C\equiv CC_6H_5)_2$	159	...	...	...	1b, 2	...	57
$\alpha\text{-}C_{10}H_7Sb(C\equiv CC_6H_5)_2$	157	...	...	...	1b, 2	...	57
$(CH_3)_2SbC\equiv CH$	...	86–88 (388)	...	...	1b	...	58
$(C_2H_5)_2SbC\equiv CH$	...	87 (79)	...	...	1b	35.5	58
$(i\text{-}C_3H_7)_2SbC\equiv CH$	...	68 (15)	...	...	1b	42.6	58
$(t\text{-}C_4H_9)_2SbC\equiv CH$	...	72 (10)	...	...	1b	45.6	58
$(CH_3)_2SbC\equiv CSb(CH_3)_2$	...	116 (17)	...	...	1a	40	58
$(C_2H_5)_2SbC\equiv CSb(C_2H_5)_2$	...	118 (1)	...	...	1b, 2	50.3	58
$(i\text{-}C_3H_7)_2SbC\equiv CSb(C_3H_7\text{-}i)_2$	...	121 (1)	...	...	1b	27.5	58
$(t\text{-}C_4H_9)_2SbC\equiv CSb(C_4H_9\text{-}t)_2$	85.5	...	...	...	1b	26.9	58
$(C_6H_5)_2SbC\equiv CSb(C_6H_5)_2$	110.5	...	...	...	1a, 2	...	48
$(p\text{-}ClC_6H_4)_2SbC\equiv CSb(C_6H_4Cl\text{-}p)_2$	149	...	...	...	1a	...	57
$(p\text{-}CH_3C_6H_4SbC\equiv CSb(C_6H_4CH_3\text{-}p)_2$	121	...	...	...	1a	...	57
$(C_6H_5)_2SbC\equiv CSb(C_6H_5)_2$	154 dec	...	...	...	1a	...	59
$[(CH_3)_3Sb^+C\equiv CSb(CH_3)_2]I^-$	110 dec	...	...	...	*a*	...	58
$[(i\text{-}C_3H_7)_2Sb^+(CH_3)C\equiv CSb(C_3H_7\text{-}i)_2]I^-$	108 dec	...	...	...	*a*	...	58
$[CH_3(C_2H_5)_2SbC\equiv CSb(C_2H_5)_2CH_3]I_2$	114 dec	...	...	...	*a*	...	58

[a] Synthesized from other acetylene compounds.

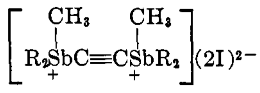
TABLE XXVI
ALKYLBISMUTH COMPOUNDS

Compound	Mp, °C	Bp (mm)	n_D^{20}	d_4^{20}	Method	Yield, %	Ref
$(p\text{-}CH_3C_6H_4)_2BiC\equiv CH$	90–91	...	...	...	1b, 2	43.2	60
$(C_6H_5)_2BiC\equiv CC_6H_5$	101	...	...	...	1a	75.3	60
$(p\text{-}CH_3C_6H_4)_2BiC\equiv CC_6H_5$	91	...	...	...	1a	83.2	60
$(p\text{-}ClC_6H_4)_2BiC\equiv CC_6H_5$	140 dec	...	...	...	1a	82.2	60
$(C_6H_5)_2BiC\equiv CBi(C_6H_5)_2$	145, 133 dec	...	...	...	1a	...	48, 60
$(p\text{-}CH_3C_6H_4)_2BiC\equiv CBi(C_6H_4CH_3\text{-}p)_2$	125 dec	...	...	...	1a	56	60
$(p\text{-}ClC_6H_4)_2BiC\equiv CBi(C_6H_4Cl\text{-}p)_2$	135 dec	...	...	...	1a, b	52.6	60

rearrangement of the ester I proceeds *via* a five-center transition state to allenylphosphonic ester II and finally a prototropic isomeric conversion to III.

D. ALKYNYL COMPOUNDS OF ARSENIC, ANTIMONY, AND BISMUTH (TABLES XXIV–XXVI)

Only a few papers have been published on the synthesis and properties of acetylenic derivatives of these elements. The strength of the metal–acetylene bond decreases from As to Bi. The oxides of alkynylarsines are still relatively stable and can often be prepared (9, 50). The antimony and bismuth compounds are so sensitive toward oxidation that it has not been possible to isolate any oxidation products containing acetylenic bonds (58). Bis(dialkylantimony) acetylide adds sulfur in ethereal solution. The sulfide, however, could not be isolated. The addition of alkyl halides leads to "onium" salt formation in the cases of alkynylarsines and alkynylantimony compounds (9, 50, 58). Bis(diethylantimony)acetylide and the isopropyl derivative are able to add 2 molar equiv of methyl iodide



$$\left[\overset{+}{\underset{}{R_2\overset{CH_3}{Sb}}}C\equiv C\overset{+}{\overset{CH_3}{Sb}}R_2\right](2I)^{2-}$$

These salts are stable in moist air (58). Bismuth compounds did not undergo any of these reactions without decomposition (60).

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