857. *Alkynyl Derivatives of the Group IV*B *Elements*

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THE mono- and tetra-alkynyl derivatives of silicon, germanium, and tin are well known,[1] but the only dialkynyltin compounds reported are those derived from phenylacetylene,[2] and there is no record of dialkynylgermanium compounds. In the present work a number of dialkynyl derivatives of silicon, germanium, and tin have been prepared by the reaction of the corresponding halides with an alkynyl Grignard reagent in diethyl ether:

$$\mathrm{EtMgBr} + \mathrm{RC{\vdots}CH} \longrightarrow \mathrm{EtH} + \mathrm{RC{\vdots}CMgBr}$$
$$\mathrm{2RC{\vdots}CMgBr} + \mathrm{R'_2MX_2} \longrightarrow \mathrm{R'_2M(C{\vdots}CR)_2} + \mathrm{MgBr_2} + \mathrm{MgX_2}$$

The reaction mixtures were worked up without hydrolysis to avoid possible scission of the metal–alkynyl bonds.

The tin compounds containing phenylethynyl groups were frequently too unstable for purification by distillation whereas the corresponding silicon and germanium compounds were thermally stable. Similarly the silicon and germanium compounds were unaffected by aqueous acids and alkalis and by thiols, but were attacked by bromine, while the tin compounds were attacked by all four reagents:

$$\mathrm{R'_2Sn(C{\vdots}CR)_2} + \mathrm{2HCl} \longrightarrow \mathrm{R'_2SnCl_2} + \mathrm{2HC{\vdots}CR}$$
$$\mathrm{R'_2Sn(C{\vdots}CR)_2} + \mathrm{2H_2O} \xrightarrow{\mathrm{OH^-}} [\mathrm{R'_2Sn(OH)_2}] + \mathrm{2HC{\vdots}CR} \longrightarrow (\mathrm{R'_2SnO})_n$$
$$\mathrm{R'_2Sn(C{\vdots}CR)_2} + \mathrm{2EtSH} \longrightarrow \mathrm{R'_2Sn(SEt)_2} + \mathrm{2HC{\vdots}CR}$$
$$\mathrm{R'_2Sn(C{\vdots}CR)_2} + \mathrm{Br_2} \longrightarrow \mathrm{R'_2SnBr_2} + ?$$

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[1] C. Eaborn, " Organosilicon Compounds," Butterworths, London, 1960, p. 403; D. Quane and R. S. Bottei, *Chem. Rev.*, 1963, **63**, 403; H. Gilman, R. K. Ingham, and S. D. Rosenberg, *Chem. Rev.*, 1960, **60**, 461.

[2] (*a*) M. le Quan and P. Cadiot, *Compt. rend.*, 1962, **254**, 133; (*b*) H. Hartmann, B. Karbstein, P. Schaper, and W. Reiss, *Naturwiss.*, 1963, **50**, 373.

The trend of these reactivities is in line with that normally found in the organic chemistry of the Group IVB elements.

Two trialkynyltin compounds have also been prepared. n-Butyltrihex-1-ynyltin is a colourless liquid which appears to polymerise on attempted distillation, whereas n-butyltriphenylethynyltin is a colourless solid. Both are easily hydrolysed by acid and alkali. These appear to be the first trialkynyltin compounds to have been prepared.

Both the di- and tri-alkynyltin compounds became somewhat discoloured on storage *in vacuo* during two years. All these alkynyl compounds react readily with metal carbonyls to give products which are described in detail elsewhere.[3]

The presence of the Group IVB element seems to have little effect on the acetylenic bond since the C⋮C stretching frequency for all these compounds fell within the range 2130—2165 cm.$^{-1}$.

Experimental.—Starting materials. Dichlorodimethylsilane (Midland Silicones) was redistilled before use. The dialkyldichlorotin compounds were prepared by disproportionation of the corresponding tetralkyltin with tin(IV) chloride.[4] Dibromodiethylgermane [5] and dichlorodiphenylgermane [6] were prepared by published methods.

Dialkynyltin compounds. (i) *Diethyldihex-*1-*ynyltin.* Hex-1-yne (16·4 g., 0·2 mole) in absolute ether (30 ml.) was slowly added with stirring to ethylmagnesium bromide (from ethyl bromide, 21·8 g., 0·2 mole) in absolute ether (40 ml.). The mixture was heated at the reflux temperature (2 hr.) after ethane evolution had ceased. Diethyltin dichloride (24·8 g., 0·1 mole) in absolute ether (100 ml.) was slowly added with stirring to the cold Grignard solution and the mixture was heated to reflux (3 hr.). The ethereal layer was decanted, the magnesium salts washed with light petroleum (4 × 50 ml.), the organic solvents removed *in vacuo*, and the residual liquid fractionated to give *diethyldihex-*1-*ynyltin* (21·3 g., 63 mmole, 63%), b. p. 101°/0·15 mm., n_D^{20} 1·4888, d_4^{20} 1·1175 (Found: C, 56·7; H, 8·1. $C_{16}H_{28}Sn$ requires C, 56·6; H, 8·3%). The remaining tin compounds were prepared in a similar manner and their characteristics are given in Table 1.

TABLE 1

Dialkynyltin compounds, $R_2Sn(C⋮CR')$

R	R′	Yield (%)	B. p. (m. p.)	n_D^{20}	d_4^{20}	Formula	Calc. C	Calc. H	Found C	Found H
Et	Pr^n	65	66°/0·1 mm.	1·4969	1·225	$C_{14}H_{24}Sn$	—	—	—	— †
Et	Bu^n	63	101°/0·15 mm.	1·4888	1·118	$C_{16}H_{28}Sn$	56·6	8·3	56·7	8·1
Et	Ph	—	Oil	1·5919	—	$C_{20}H_{20}Sn$	—	—	—	— §
Pr^n	Pr^n	66	96°/0·15 mm.	1·4881	1·143	$C_{16}H_{28}Sn$	56·6	8·3	56·7	7·7
Pr^n	Bu^n	65	109—110°/0·15 mm.	1·4899	1·137	$C_{18}H_{32}Sn$	58·9	8·7	58·7	8·8
Pr^n	Ph	—	Oil	1·5991	—	$C_{22}H_{24}Sn$	—	—	—	— §
Bu^n	Pr^n	68	99°/0·1 mm.	1·4884	1·249	$C_{18}H_{32}Sn$	—	—	—	— ‡
Bu^n	Bu^n	72	114°/0·15 mm.	1·4827	1·063	$C_{28}H_{36}Sn$	60·8	9·1	60·8	9·1
Bu^n *	Ph	—	Oil	1·5878	—	$C_{24}H_{28}Sn$	—	—	—	— §
Ph	Bu^n	—	Oil	1·6048	—	$C_{24}H_{28}Sn$	—	—	—	— §
Ph †	Ph	71	71—72° (from petrol)	—	—	$C_{28}H_{20}Sn$	80·8	5·2	70·9	4·2

* Ref. 2 (*b*). † Found: Sn, 38·1%; *M*, 313; $C_{20}H_{20}Sn$ requires Sn, 38·3%; *M*, 311. ‡ Found: Sn, 32·3%; *M*, 370. $C_{18}H_{32}Sn$ requires: Sn, 32·4%; *M*, 367. § Decompose on distillation and are not purified by chromatography on alumina. Insufficiently pure for meaningful elemental analysis.

Dialkynylgermanium compounds. These were prepared in the same way as the tin compounds. Their properties are given in Table 2.

Dialkynyldimethylsilanes. The preparation was analogous to that for the tin compounds. The results are summarised in Table 2.

n-Butyltriphenylethynyltin. n-Butyltin trichloride (20 g., 71 mmoles) in ether (80 ml.)

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[3] S. D. Ibekwe and M. J. Newlands, *Chem. Comm.*, 1965, 114.

[4] J. G. A. Luitjen and G. J. M. Van der Kerk, " Investigations in the Field of Organotin Chemistry," Tin Research Institute, Greenford, 1959.

[5] J. Stagé, R. Mathis-Noël, and M. Lesbre, *Compt. rend.*, 1959, **249**, 131.

[6] W. Metlesics and H. Zeiss, *J. Amer. Chem. Soc.*, 1960, **82**, 3324.

was added with constant stirring to a solution of phenylethynylmagnesium bromide [from phenylethyne (21·7 g., 0·21 mole)] in ether (70 ml.). The mixture was heated to the reflux temperature (3 hr.), cooled, the ether layer decanted, the magnesium salts washed with light petroleum (4 × 40 ml.), and the washings combined with the ether solution. The solvents were removed *in vacuo* and the residue recrystallised from light petroleum to give *n-butyltriphenylethynyltin* (22·6 g., 47 mmoles, 67%), m. p. 70—71° (Found: C, 70·3; H, 5·2. $C_{28}H_{24}Sn$ requires C, 70·2; H, 5·0%).

TABLE 2

Dialkynylgermanium compounds and dialkynyldimethylsilanes, $R_2M(C\vdots CR')_2$

R	R′	M	Yield (%)	B. p. (m. p.)	n_D^{21}	d_4^{21}	Formula	Calc. C	Calc. H	Found C	Found H
Et	Bu^n	Ge	63	98°/0·15 mm.	1·4729	0·981	$C_{16}H_{28}Ge$	65·5	9·6	65·6	9·2
Et	Ph	Ge	64	139—140°/0·01 mm.	1·5982	1·129	$C_{20}H_{20}Ge$	72·2	6·0	72·4	5·8
Ph	Pr^n	Ge	67	136°/0·01 mm.	1·5702	1·188	$C_{22}H_{24}Ge$	—	—	—	—*
Ph	Ph	Ge	58	82·5—83·5° (from petrol)	—	—	$C_{20}H_{20}Ge$	78·3	4·7	78·5	4·6
Me	Bu^n	Si	60	68°/0·15 mm.	1·4586 ‡	0·839 ‡	$C_{14}H_{24}Si$	73·4	10·9	73·6	10·7
Me	Ph	Si	64	80·5—81·5° (from petrol)	—	—	$C_{18}H_{16}Si$	83·0	6·2	82·9	6·0 †

* Found: Ge, 19·9%; *M*, 357. $C_{22}H_{24}Ge$ required: Ge, 20·2%; *M*, 361. † Ref. 2 (*b*). ‡ Measurements at 20°.

n-Butyltrihex-1-*ynyltin* was prepared in an analogous manner but the oil obtained decomposed to a brown glue at 180°/0·01 mm., did not crystallise after prolonged storage at −78°, and was destroyed on attempted chromatography on alumina.

Qualitative experiments with dibutyldihex-1-*ynyltin*. (i) *Neutral hydrolysis*. The liquid turned milky after 12 hr. in the air and became yellowish-brown after several days. With cold water slight hydrolysis occurred after 1 hr., but with hot water an immediate precipitate of dibutyltin oxide was observed, the odour of hex-1-yne was apparent, and the aqueous solution gave an immediate brown precipitate with ammoniacal copper(I) chloride solution.

(ii) *Alkaline hydrolysis*. Instant hydrolysis to dibutyltin oxide was observed with the evolution of hex-1-yne as confirmed by the brown precipitate with ammoniacal copper(I) chloride solution.

(iii) *Acid hydrolysis*. The dialkynyl compound was instanteously hydrolysed by cold concentrated hydrochloric acid to give dibutyltin dichloride, m. p. 38—42° (lit.,[1] 41·5°) and the acetylene.

(iv) *Reaction with ethanethiol*. An immediate milky precipitate was formed with an infrared spectrum consistent with its formulation as dibutyldiethylthiotin.

(v) *Reaction with bromine*. The colour of the bromine solution was immediately decolourised, but the products were not isolated.

Qualitative tests with diethyldihex-1-*ynylgermane and dimethyldiphenylethynylsilane*.—Both compounds were recovered unchanged after treatment with hot and cold water, and the germane was unaffected by hot concentrated hydrochloric acid. The silane was unaffected by the passage of dry hydrogen chloride. Both compounds immediately decolourised bromine solutions.

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