Organometallic Diazoalkanes. Part I. Synthesis and Characterisation of Simple Group IVB Organometallic Diazomethanes, and the Tin–Carbon Cleavage Reactions of Bis(trimethylstannyl)diazomethane

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The synthesis and characterisation of the Group IVB organometallic diazomethanes is described. The compounds prepared were $Me_3Si{\cdot}CHN_2$, $(Me_3M)_2CN_2$ (M = Ge, Sn, or Pb), $Me_3Si(Me_3Sn)CN_2$, $(Ph_3Ge)_2CN_2$, and $(R_3Sn)_2CN_2$ (R = Et, Bu^n, or Ph). Two preparative methods have been explored: from diazomethane and the metal amide $R_3M{\cdot}NMe_2$, and from diazomethyl-lithium and the appropriate chloride; their scope and limitation is discussed. The compounds are volatile, non-explosive, photosensitive, and reactive. Six Sn–C cleavage reactions of $(Me_3Sn)_2CN_2$ are described; nitrogen is generally lost and the carbene $(Me_3Sn)_2C$: may be an intermediate.

In 1967 we reported, in preliminary form, the synthesis [equations (1) and (2)] and characterisation of trimethylsilyl- ($Me_3Si{\cdot}CHN_2$) and trimethylstannyl-diazomethane.[1] The features of interest appeared to be that these compounds were (i) the first volatile covalent organometallic diazoalkanes, (ii) relatively stable with respect to heat, and (iii) highly chemically reactive. An improved synthesis of the silicon compound was subsequently described which used the action of base on the appropriate *N*-nitroso-compound, $Me_3Si{\cdot}CH_2{\cdot}N(NO){\cdot}CONH_2$.[2] The structure of the tin compound was established as $(Me_3Sn)_2CN_2$.[3] The silicon and the tin compound have proved to behave chemically in many respects as 1,3-dipoles.[3,4] The present paper reports the synthesis and characterisation of a range of simple Group IVB organometallic diazomethanes and the extensive Sn–C cleavage reactions of bis(trimethylstannyl)diazomethane.

Apart from the compounds in Table 1, the organometallic diazoalkanes previously known were the following: $LiCHN_2$,[5] $NaCHN_2$ (not isolated),[6] $AgC(N_2){\cdot}COR$

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[1] M. F. Lappert and J. Lorberth, *Chem. Comm.*, 1967, 836.

[2] D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Amer. Chem. Soc.*, 1968, **90**, 1080.

[3] M. F. Lappert and J. S. Poland, *Chem. Comm.*, 1969, 156.

[4] M. F. Lappert and J. S. Poland, *Chem. Comm.*, 1969, 1061.

[5] E. Müller and D. Ludsteck, *Chem. Ber.*, 1954, **87**, 1887; E. Müller and W. Rundel, *ibid.*, 1955, **88**, 917; 1957, **90**, 1299, 1302, 2673.

[6] E. Müller and H. Disselhoff, *Naturwiss.*, 1933, **21**, 661; *Annalen*, 1934, **512**, 250; E. Müller and W. Kreutzmann, *Annalen*, 1934, **512**, 264.

(not isolated) (R = OEt,[7] alkyl,[8] or aryl), $Cd(CHN_2)_2$ (not isolated),[9] $Hg[C(N_2)R]_2$ (R = H,[10] ROCO,[11] or ArCO [12]), $R^1{}_3Si{\cdot}C(N_2)R^2$,[13,14] $R_3Si{\cdot}C(N_2){\cdot}CO_2Et$,[15,16] $Ph_3Ge{\cdot}C(N_2)Ph$,[13] $R_3Sn{\cdot}C(N_2){\cdot}CO_2Et$,[15,17] and $R_2Sn[C(N_2){\cdot}CO_2Et]_2$.[17] The preparative methods which have been employed used the following starting materials: (*a*) a diazoalkane [with a metal alkyl (alkane elimination), oxide (H_2O elimination), or acetate (methyl acetate elimination)], (*b*) *p*-toluenesulphonyl azide [*e.g.*, $Me_3Si{\cdot}CH_2Ph + p\text{-}Me{\cdot}C_6H_4{\cdot}SO_2N_3 \xrightarrow{Bu^nLi/TMEDA} Me_3Si{\cdot}C(N_2)Ph$], (*c*) a lithium, silver, or mercury(II) diazomethane [*e.g.*, $Hg\{C(N_2){\cdot}CO_2Et\}_2 + (Ph_3Sn)_2S \longrightarrow 2Ph_3Sn{\cdot}C(N_2){\cdot}CO_2Et$], (*d*) a suitable *N*-nitroso-compound or hydrazone [*e.g.*, $Me_3Si{\cdot}COPh \xrightarrow[\text{or (i) } p\text{-}Me{\cdot}C_6H_4{\cdot}SO_2NH{\cdot}NH_2\text{, (ii) NaOMe}]{\text{(i) } N_2H_4\text{, (ii) } MnO_2} Me_3Si{\cdot}C(N_2)Ph$], and (*e*) nitrous oxide or nitrosyl chloride (for $LiCHN_2$ using MeLi or MeNHLi, respectively.) Organometallic diazoalkanes were intensely coloured and ranged from yellow to red. Their stability appears to be related to steric considerations and the nature of the substituent groups; the monosubstituted diazomethanes are the least stable, with the sodium and mercury(II) salts dangerously explosive and the lithium salt exploding in air when dry. All are photosensitive.

TABLE 1

Some properties of the Group IVB organometallic diazomethanes

Compound	Preparative route [a]	Yield (%)	B.p. (°/mm.)	M.p. (°)	$\nu(N{\equiv}N)$ (cm.$^{-1}$)	τ (Me_3M) [b]	Dipole moment [c] (D)
$Me_3Si{\cdot}CHN_2$	(2)	5	42—45/128		2070 [d]	10·02	
$Me_3Si(Me_3Sn)CN_2$	(1)	86	44—46/0·5		2022 [d]	9·88 (Si), 9·73 (Sn)	
$(Me_3Ge)_2CN_2$	(1)	58	45—47/100		2050 [d]	9·85 (Ge)	
$(Ph_3Ge)_2CN_2$	(2)	44		155—156	2032 [e]		
$(Me_3Sn)_2CN_2$	(1) (2)	95 80	64—67/0·1		2000 [d]	9·53 [f]	2·02
$(Et_3Sn)_2CN_2$	(1)	82	110—112/0·01		1995 [d]	(CH_2,9·04,CH_3, 8·79) [g]	2·12
$(Bu^n{}_3Sn)_2CN_2$	(1)	46	145—148/0·01		1995 [d]	(Multiplet, not resolved)	2·52
$(Ph_3Sn)_2CN_2$	(1) (2)	90 56		127—130 (decomp.)	2002 [e]		
$(Me_3Pb)_2CN_2$	(1)	100 [i]	decomp.		1950 [d]	9·28 [h]	
$(Me_3Ge)CN_2(CO_2Et)$	(1)	100 [i]	85/10		2078		

[a] The number in this column refers to the appropriate equation in the text. [b] 10% Solution in C_6H_6. [c] In C_6H_6 at 20°. [d] Capillary film. [e] 'Nujol' mull. [f] $J_{^{117}Sn-^1H}$, 53·5 and $J_{^{119}Sn-^1H}$ 56·0 Hz. [g] $J_{^{117}Sn-CH_3}$ 78 and $J_{^{119}Sn-CH_3}$ 82 Hz. [h] $J_{^{208}Pb-^1H}$ 62·5 Hz. [i] Yields here refer to undistilled material.

The new diazo-compounds and some of their physical properties are shown in Table 1. They have been prepared by two routes: by dimethylamine elimination [equation (1), M = Ge, Sn, or Pb; R^2 = Me or $SiMe_3$] or by lithium salt elimination [*e.g.*, equation (2)]; all compounds except $Me_3Si{\cdot}CHN_2$ have the formula R_2CN_2 (*i.e.*, they are disubstituted diazomethanes) as shown by their analyses (*e.g.* Table 2), spectra and reactions. No

$$2R^1{}_3M{\cdot}NR^2{}_2 + CH_2N_2 \longrightarrow (R^1{}_3M)_2CN_2 + 2HNR^2{}_2 \quad (1)$$

$$2Ph_3GeCl + 2Li(CHN_2) \longrightarrow (Ph_3Ge)_2CN_2 + 2LiCl \quad (2)$$

reaction was observed when chlorotrimethylsilane and ethyl diazoacetate were heated in refluxing ether in the presence of an amine. Transmetallation reactions have, thus far, been unsuccessful; for example equation (3) has not been established, but mixing the reagents in dichloromethane at —30° yielded a dark-brown solution (and no gas evolution) with i.r. characteristics appropriate to a boryl diazoacetate [ν(N≡N), 2075 cm^{-1}; ν(CO), 1675 cm.$^{-1}$].

$$Me_3Sn{\cdot}C(N_2){\cdot}CO_2Et + Bu^n{}_2BCl \not\longrightarrow Bu^n{}_2B{\cdot}C(N_2){\cdot}CO_2Et + Me_3SnCl \quad (3)$$

TABLE 2

Analytical data for some distannyldiazomethanes

	Found (%) [a]				Required (%)		
Compound	C	H	N	Formula	C	H	N
$(Et_3Sn)_2CN_2$	22·0	7·9	7·4	$C_{13}H_{30}N_2Sn_2$	21·9	7·85	6·9
$(Bu^n{}_3Sn)_2CN_2$	48·4	8·7	4·5	$C_{25}H_{54}N_2Sn_2$	48·4	8·7	3·8
$(Ph_3Sn)_2CN_2$	59·6	4·05	3·8	$C_{37}H_{30}N_2Sn_2$	59·9	4·05	3·45

[a] Nitrogen analyses were obtained by use of vacuum line techniques with a Töpler pump.

The Amine Elimination Procedure.—Mechanistically, this synthesis [equation (1)] may belong to the type of reaction described by equation (4) (in which L represents

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[7] U. Schöllkopf and N. Rieber, *Angew. Chem. Internat. Edn.*, 1967, **6**, 261.

[8] U. Schöllkopf and N. Rieber, *Chem. Ber.*, 1969, **102**, 488.

[9] T. DoMinh, O. P. Strausz, and H. E. Gunning, *Tetrahedron Letters*, 1968, 5237.

[10] A. N. Wright, K. A. W. Kramer, and G. Steel, *Nature*, 1963, **199**, 903.

[11] E. Buchner, *Ber.*, 1895, **28**, 215.

[12] P. Yates and F. Garneau, *Tetrahedron Letters*, 1967, 71.

[13] A. G. Brook and P. F. Jones, *Canad. J. Chem.*, 1969, **47**, 4353.

[14] K. D. Kaufmann, B. Auräth, P. Träger, and K. Rühlmann, *Tetrahedron Letters*, 1968, 4973.

[15] U. Schöllkopf and N. Rieber, *Angew. Chem. Internat. Edn.*, 1967, **6**, 884.

[16] K. D. Kaufmann and K. Rühlmann, *Z. Chem.*, 1968, **8**, 262.

[17] J. Lorberth, *J. Organometallic Chem.*, 1968, **15**, 251.

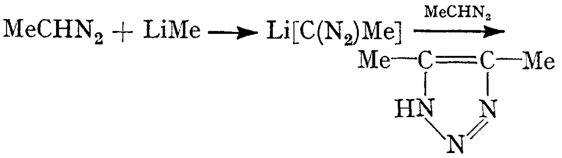
the sum of all ligands other than one NR_2 group attached to the metal or metalloid M), recognized in 1964 for a wide range of protic compounds HA, especially for amides of the more electropositive metals such as Sn^{IV}.[18] Since diazomethane reacts with lithium alkyls to yield alkanes and diazomethyl-lithium $LiCHN_2$,[5] it certainly has protic character. Moreover an electron-releasing (*e.g.*, X = Me) substituent at carbon decreases the reactivity of $XCHN_2$,[19] while an electron-withdrawing substituent (*e.g.*, X = CO_2Et) [17] has the converse effect, with respect to reactions with tin amides. A limitation on the amine elimination method is that while the germanium and tin amides, and also the lead compound $Me_3Pb{\cdot}N(SiMe_3)_2$ (see also ref. 20), react (see Table 1) with diazomethane, amides of boron ($Ph_2B{\cdot}NMe_2$) and silicon ($Me_3Si{\cdot}NMe_2$) did not react, even with the more powerful reagent ethyl diazoacetate. With $Me_3Ge{\cdot}NMe_2$ rather more vigorous conditions were required than with $Me_3Sn{\cdot}NMe_2$: the reactivity sequence therefore appears to be: $Si \ll Ge < Sn < Pb$. An alternative model for equation (1) is that the reaction is a two-step process, involving initial 1,3-insertion [equation 5(*a*)] and subsequent elimination [equation 5(*b*)]; insertion reactions into Sn–N bonds are well-known [21] and diazoalkanes are capable of behaving as 1,3-dipoles.[1-4, 22]

$$LM{-}NMe_2 + HA \longrightarrow LM{-}A + Me_2NH \qquad (4)$$

$$\begin{tikzcd}
Me_3Sn{-}NMe_2 + \bar{C}H_2{-}N{=}\overset{+}{N} \arrow[r, "(a)"] & & \\
 & Me_3Sn{\cdot}CH_2{-}N{=}N{-}NMe \arrow[r, "(b)"] & Me_3Sn{\cdot}CHN_2 \arrow[dl, "Me_3Sn{\cdot}NMe_2"', "(a)"] \\
(Me_3Sn)_2CN_2 & (Me_3Sn)_2CH{-}N{=}N{-}NMe_2 \arrow[l, "(b)"'] &
\end{tikzcd} \qquad (5)$$

A curious feature is that for Sn a monosubstituted compound (*e.g.*, $Me_3Sn{\cdot}CHN_2$) was not isolable. For example, even when using a molar ratio of diazomethane to tin amide greater than 3 : 1, the only tin-containing product isolated was bis(trimethylstannyl)diazomethane. In terms of the mechanism according to equation (4), this is not readily explicable, since it would be necessary to postulate that the reactivity, and hence probably the acidity, of diazomethane is less than that of trimethylstannyldiazomethane; while it is established that trimethylstannyl is among the most powerful of electron-releasing groups.[23] According to equation (5), however, the necessary corollary is that a trimethylstannyl substituent makes diazomethane into a more effective 1,3-dipole. There is evidence that this is the case for bis(trimethylstannyl)diazomethane,[2,3] and this may be rationalised by invoking either *d*-orbital participation or by the ionicity of the Sn–C bond for delocalisation of the negative charge on the carbon of $(Me_3Sn)_2\bar{C}{-}N{=}\overset{+}{N}$.

The Salt Elimination Procedure.—This [equation (2)] is limited by the availability of lithium reagents. For example, $LiC(N_2)Me$ has not yet been prepared; if formed it reacts with diazoethane [equation (6)].[24] The



(6)

ligand CHN_2^- could not be co-ordinated to a transition metal to form a stable complex; reactions of $LiCHN_2$ and various transition-metal halides gave products which were not identified.

The reactions of the lithium salt with alkyl halides were examined. The expectation was that the lithium halide elimination reaction would provide a convenient synthesis for higher diazoalkanes. However, only the aprotic compounds R_2CN_2 were isolated. A possible explanation is that the initial mono-substituted diazomethane is further lithiated and then inevitably reacts with another mole of halide [equation (7)]. The

$$LiCHN_2 + RX \longrightarrow RCHN_2 \xrightarrow[(-HA)]{LiA} Li[C(N_2)R] \xrightarrow{RX} R_2CN_2 + LiX \qquad (7)$$

lithiating agent LiA in the second step may be either diazomethyl-lithium or unreacted methyl-lithium. The latter reagent may be present if polymethylene is formed in the reaction of methyl-lithium with diazomethane (*i.e.*, if less than stoicheiometric quantities of diazomethane are present). It is also possible that diazomethyl-lithium reacts in the sense of equation (8).

$$MeLi + LiCHN_2 \longrightarrow Li_2CN_2 + CH_4 \xrightarrow{2RX} R_2CN_2 + LiX \qquad (8)$$

Silicon appears to be unique within Group IVB in forming a stable monosubstituted compound $Me_3M{\cdot}CHN_2$ (M = Si). Conversely, it is the only member of the Group not to form a bis-compound $(Me_3Si)_2CN_2$, which is a diazoalkane. Scherer and Schmidt have previously reported [25] that interaction of chlorotrimethylsilane (2 moles) and diazomethyl-lithium (1 mole) gives a product of empirical formula $(Me_3Si)_2CN_2$ (*ca.* 25%), which does not show i.r. absorption in the range 2900—1500 cm.$^{-1}$. This observation has now been confirmed. The Raman spectrum of the compound, b.p. 76—79°/10 mm., also failed to show a line in the same region of the spectrum. The mass spectrum showed the presence of a unipositive ion at mass 357, which corresponds to a dimeric parent ion −15; however, molecular-weight determination in benzene was consistent with a monomer (Found: *M*, 168. Calc. for $C_7H_{18}N_2Si_2$: *M*, 186). A dimeric

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[18] K. Jones and M. F. Lappert, *Proc. Chem. Soc.*, 1964, 22; *J. Organometallic Chem.*, 1965, **3**, 295.

[19] M. F. Lappert and J. S. Poland, unpublished work.

[20] J. Lorberth, to be published.

[21] *Cf.* M. F. Lappert and B. Prokai, *Adv. Organometallic Chem.*, 1967, **5**, 225.

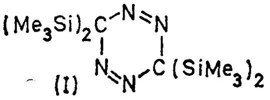
[22] *Cf.* R. Huisgen, *Angew. Chem.*, 1963, **75**, 604.

[23] R. W. Bott, C. Eaborn, and D. R. M. Walton, *J. Organometallic Chem.*, 1964, **2**, 154.

[24] E. Müller and W. Rundel, *Chem. Ber.*, 1956, **89**, 1065.

[25] O. J. Scherer and M. Schmidt, *Z. Naturforsch.*, 1965, **20b**. 1009.

structure (I) would result from head-to-tail 1,3-dipolar association of two units of monomer. Such a compound might well have its highest i.r. absorption [from ν(CH_3)] at *ca.* 1500 cm.$^{-1}$. The reason that the silicon compound may be the only member in the series $(Me_3M)_2CN_2$ to dimerise thus might be explained by the more effective delocalisation of the negative charge from carbon to the metal (if other than M = Si) for the structure $Me_3\bar{M}{-}\bar{C}{-}N{=}\overset{+}{N}$; certainly the ions Me_3Sn^- and Me_3Pb^- are well-known, while Me_3Si^- is only formed under rather special conditions.



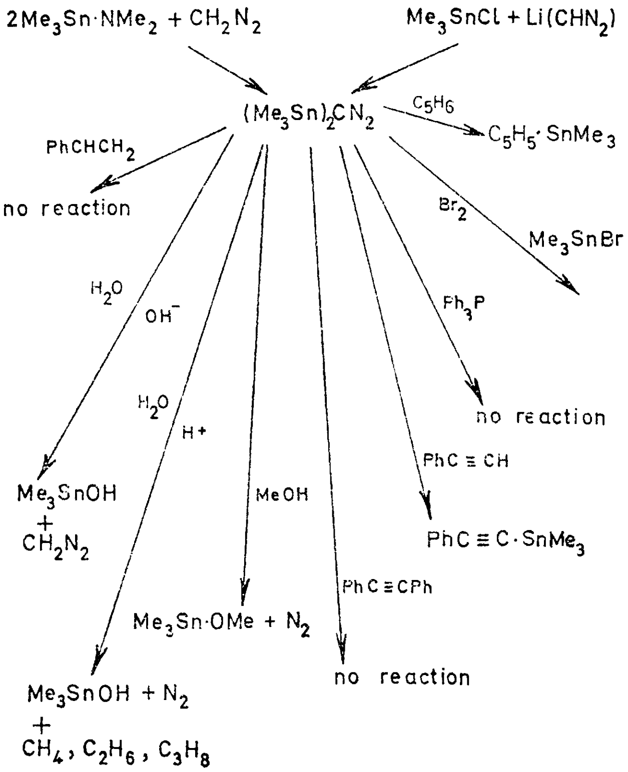
(I)

By use of less than an equimolar ratio of chlorotrimethylsilane to the lithium salt, a low yield of trimethylsilyldiazomethane was obtained, with the bis-compound as the major product.

Properties.—All compounds were stable with respect to explosive decomposition, but were light-sensitive and therefore were stored in the dark at −20°. The chemistry of the trimethyltin derivative was investigated; this compound appeared to be the most reactive. The trimethyl-, triethyl-, and tri-n-butyl-tin compounds are all extremely air-sensitive, but bis(triphenylstannyl)-diazomethane is only air-sensitive in solution and the germanium and silicon compounds are air-stable.

The analyses, physical properties, and reactions of the stannyldiazomethane led to its formulation as $(Me_3Sn)_2CN_2$;[3] the formula $Me_3Sn{\cdot}CHN_2$ originally proposed[1] was found to be incorrect. The following points in this paragraph support the present structural assignment. (i) The synthesis of heterocycles, by 1,3-cycloaddition to the tin diazomethane, shows these to contain two trimethyltin groups.[3] (ii) The ^1H n.m.r. spectrum of the diazomethane shows only one signal (no α-proton signal). (iii) The i.r. absorption at 2000 cm.$^{-1}$ is lower than might have been expected for a mono-substituted derivative; the R_3Sn group in similar compounds has been shown to lower ν(N≡N) with respect to the parent compound by 35—40 cm.$^{-1}$. (iv) Molecular-weight measurements gave values in the region 330—380 [$(Me_3Sn)_2CN_2$ requires *M*, 366]; the values tended to vary slightly due to hydrolysis of the very air-sensitive compound. (v) The preparation of the diazomethane was performed with the ratio 2 : 1 appropriate to equation (1), and the yield based on $(Me_3Sn)_2CN_2$ corresponded to 95%. (vi) Analyses of the compound, and of its homologues, using freshly distilled samples, supports the formulation as $(Me_3Sn)_2CN_2$; nitrogen estimations proved troublesome, and the quoted figures represent vacuum-line estimations, collecting the permanent gases by means of a Töpler pump, with subsequent g.l.c. and mass spectrometric analysis. (vii) The Sn–C cleavage reactions of bis(trimethylstannyl)diazomethane, which are summarised in the Scheme, provided further support.

As regard (vii), the reaction with acid is particularly informative. The total volume of gas evolved appeared to agree with the formula $Me_3Sn{\cdot}CHN_2$ when the gas was assumed to be only nitrogen. G.l.c. determinations, however, showed the gas to contain only 64% nitrogen, the other gases being methane, ethane, and propane. Thus, on the basis of the formula $(Me_3Sn)_2CN_2$, the actual yield of nitrogen corresponds to 98% of the theoretical.



SCHEME Sn–C Cleavage reactions of $(Me_3Sn)_2CN_2$

The structure of the trimethylstannyldiazomethane is believed to be $(Me_3Sn)_2CN_2$ (II), rather than $Me_3Sn\bar{C}{=}\overset{+}{N}{=}NSnMe_3$ (III) or $\bar{C}{\equiv}\overset{+}{N}{-}N(SnMe_3)_2$ (IV). The evidence is: (i) the syntheses of heterocycles by 1,3-cycloaddition precludes the possibility of structure (IV);[3] (ii) variable-temperature n.m.r. spectroscopy did not affect the trace [structure (III) would be expected to give two signals, at any rate at low temperature]; (iii) the synthesis according to equation (1); and (iv) the n.m.r. coupling between Sn and C nuclei.

The reaction of the compound with phenylacetylene might be considered as appropriate for structure (IV) [see, equation (4); *i.e.*, an Sn–N compound might have been expected to behave towards PhC⋮CH as does[18] $Me_3Sn{\cdot}NMe_2$]. However, it is assumed that in (II) the tin–carbon bond is highly reactive owing to the neighbouring electronegative group; thus, the compounds $R_3Sn{\cdot}CH_2{\cdot}COCH_3$ hydrolyse instantly.[26]

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[26] I. F. Lutsenko, S. V. Ponomarev, and O. P. Petrii, *Zhur. obshchei Khim.*, 1962, **32**, 896.

It is likely that the reactions shown in the Scheme involve a distannylcarbene intermediate. The reasons are that (i) diazoalkanes are known to decompose in this way, (ii) trimethylsilyldiazomethane has been established as a silylcarbene precursor,[2] and (iii) it is difficult otherwise to account for the multiplicity of products obtained upon Sn–C cleavage: *cf.*, the reaction with aqueous acid to yield lower paraffins.

From Table 1, it will be seen that the position of $\nu(N\equiv N)$ in $XCHN_2$ and X_2CN_2 progressively decreases in the series $X = H > Me_3Si > Me_3Ge > Me_3Sn > Me_3Pb$, as is consistent with progressive electron-release of X. The position of the ^1H n.m.r. chemical shift in the series $XCHN_2$ as decreasing from $\tau = 7{\cdot}77$ in $Me_3Si{\cdot}CHN_2$, 6·92 in CH_2N_2,[27] 4·98—4·57 in $ArSO_2CHN_2$,[28] and 4·0 in O_2NCHN_2 [29] may be understood similarly.

EXPERIMENTAL

Manipulations were carried out under dry oxygen-free nitrogen. I.r. spectra were recorded with Perkin-Elmer 225, 237, and 337 instruments (as liquid films or ' Nujol ' mulls). ^1H n.m.r. spectra were measured on Varian A60 and HA 100 instruments. Dipole moments were measured on a DM 01 WTW Dipolemeter. Mass spectra were obtained on Atlas CH_4 and A.E.I. M.S.9 instruments.

Synthesis of Organometallic Diazomethanes by Amine Elimination.—Diazomethane (2·43 g., 0·6 mol.) was distilled (20°/0·01 mm.) (with ether) from an ethereal solution onto dimethylaminotrimethylstannane (20·0 g., 1 mol.) in ether (50 ml.) at −196°. The detailed procedure was to cool a flask of ethereal diazomethane to −196°, then evacuate to 0·01 mm. on the vacuum line; the system was closed and the cooling bath was removed from the original flask while cooling the dimethylaminotrimethylstannane receptacle to −196°. The reactants were allowed to warm to room temperature under nitrogen and with stirring (2 hr.). Excess of diazomethane and ether were removed under vacuum and distillation of the remaining liquid gave *bis(trimethylstannyl)diazomethane* (16·8 g., 95%), b.p. 64—67°/0·1 mm. [Found: C, 22·8; H, 5·0; N, 6·5%; *M*, (osmometrically, 352) (cryoscopically, 360). $C_7H_{18}N_2Sn_2$ requires C, 22·9; H, 4·95; N, 7·6%; *M*, 367]. The other compounds $(R_3Sn)_2CN_2$ (R = Et, Bu^n, or Ph) synthesised by this method were similarly prepared, as summarised in Tables 1 and 2.

Dimethylaminotrimethylgermane (8·0 g., 1 mol.) in ether was added to an ethereal solution of diazomethane (4·0 g., 2 mol.); the total volume of solvent was 100 ml. After refluxing (3 hr.), distillation afforded the bright yellow bis(trimethylgermyl)diazomethane (3·90 g., 58%), b.p. 45—47°/100 mm. The compound was not completely pure; the ^1H n.m.r. showed the presence of a trace of $Me_3Ge{\cdot}NMe_2$.

Dimethylaminotrimethylstannane (2·54 g., 1 mol.) in ether (10 ml.) was added dropwise to trimethylsilyldiazomethane (1·54 g., 1·1 mol.) in ether (55 ml.) with stirring at 0°. The reactants were allowed to warm to room temperature while being stirred (2 hr.). After removal of solvent, distillation afforded *trimethylsilyl(trimethylstannyl)diazomethane* (2·9 g., 86%), b.p. 44—46°/0·5 mm. (Found C, 29·9; H, 6·45. $C_7H_{18}N_2SiSn$ requires C, 30·3; H, 6·55%).

By use of a similar procedure, bis(trimethylsilyl)aminotrimethylplumbane (8·0 g.) and diazomethane in ether (excess) afforded a bright yellow, viscous liquid which decomposed instantly upon attempted distillated under high vacuum. However, it is believed to be bis(trimethylplumbyl)diazomethane on the basis of the i.r. and ^1H n.m.r. data cited in Table 1 and the mass spectrum; this shows, as the highest mass peak an ion of $m/e = 518$ (for ^{208}Pb), which corresponds to (parent $-28)^+$, assigned as $(Me_3Pb)_2C^+$.

Synthesis of Organometallic Diazomethanes by the Salt Elimination Reactions.—Diazomethane (2·06 g., 1 mol.) was distilled under vacuum from an ethereal solution onto methyl-lithium (1·15 g., 1 mol.) in ether (50 ml.) cooled to −196°. The mixture was allowed to warm to ambient temperature and was stirred magnetically (2 hr.) under nitrogen. The yellow colour of the diazomethane disappeared. The product was cooled to −196° and chlorotrimethylstannane (9·91 g., 1 mol.) was distilled in under vacuum. The mixture was allowed to warm to room temperature and was stirred (2 hr.), affording a white precipitate and deep-yellow solution. The mixture was then concentrated to 40 ml., by removal of volatiles under vacuum, and was filtered. The filtrate was distilled to yield, after removal of ether, bis(trimethylstannyl)diazomethane (7·25 g., 80%), b.p. 64—67°/0·1 mm. (Found: C, 22·9; H, 4·96%).

Diazomethane (0·84 g., 1 mol.) in ether (110 ml.) was added (10 min.) to methyl-lithium (0·44 g., 1 mol.) in ether (20 ml.), with stirring at −78°. The mixture was allowed to warm to room temperature and was stirred (1 hr.). A slurry of bromotriphenylstannane (8·62 g., 1 mol.) in ether (150 ml.) was added to the product at −30°. The resulting mixture was allowed to warm to room temperature and was stirred (3 hr.). All volatiles were then removed and the resulting solid was dried under high vacuum. Ether (100 ml.) was added and the product was filtered. Light petroleum (100 ml.) was added to the filtrate which was stored (48 hr.) at −20°. *Bis(triphenylstannyl)diazomethane* (4·1 g., 56%) (Found: C, 58·8; H, 4·05; N, 3·7. $C_{37}H_{30}N_2Sn_2$ requires C, 59·9; H, 4·1; N, 3·75%), m.p. 127—130° (decomp.), was precipitated as yellow crystals, which were filtered off and dried under vacuum.

The same procedure, with diazomethane (1·62 g., 1 mol.) in ether (170 ml.), methyl-lithium (0·85 g., 1 mol.) in ether (50 ml.), and chlorotriphenylgermane (13·0 g., 1 mol.) in ether (150 ml.), and subsequent recrystallisation from ether–light petroleum at −20° gave yellow crystals of *bis(triphenylgermyl)diazomethane* (5·4 g., 44%), m.p. 155—156° [Found: C, 68·1; H, 4·65; N, 4·2%; *M* (osmometrically), 637. $C_{37}H_{30}Ge_2N_2$ requires C, 68·6; H, 4·65; N, 4·3%; *M*, 648].

Sn–C *Cleavage Reactions of Bis(trimethylstannyl)diazomethane.*—(a) *With aqueous hydrochloric acid.* Excess of hydrochloric acid (1·0M, 10 ml.) was added dropwise to bis(trimethylstannyl)diazomethane (1·660 g.) and the temperature was kept below 10°. A violent reaction took place and a gas (157 ml. at 760 mm.) was given off. This gas was identified by g.l.c., using a gas density balance, to contain nitrogen (0·128 g., 65·0%), methane (14·4%), ethane (12·3%), and propane (8·3%) [$(Me_3Sn)_2CN_2$ requires

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[27] A. Ledwith and E. C. Friedrich, *J. Chem. Soc.*, 1964, 504.

[28] A. M. van Leusen and J. Strating, *Rec. Trav. chim.*, 1965, **84**, 151.

[29] U. Schöllkopf and P. Markusch, *Tetrahedron Letters*, 1966, 6199.

nitrogen, 0·127 g.]. The residue was trimethyltin hydroxide (1·54 g., 95%), m.p. 180° (decomp.), identified by its i.r. spectrum (comparison with an authentic sample).

(b) *With methanol.* Excess of methanol (10 ml.) was added dropwise to bis(trimethylstannyl)diazomethane (3·10 g.) in a flask attached *via* a trap (—196°) to a gas burette. A non-condensable gas (162 ml.) was evolved [$(Me_3Sn)_2CN_2$ requires N_2, 189 ml.]. Distillation of the residue yielded methoxytrimethylstannane (2·9 g., 89%), identified by i.r. and ^1H n.m.r. spectra (as compared with an authentic sample).

(c) *With alkali.* Excess of conc. potassium hydroxide solution was added dropwise to bis(trimethylstannyl)diazomethane (3·129 g.) in ether (25 ml.) at 0°. The yellow ethereal layer became a darker yellow; volatiles were removed under vacuum until the residual ethereal layer was colourless. The distillate was identified as diazomethane [i.r. solution spectrum: $\nu(N\equiv N)$, 2088 cm.$^{-1}$]; it was treated with benzoic acid (1·5777 g.) in ether (50 ml.); the diazomethane (Found: 0·312 g., 88%) was estimated by back titration of excess of acid. Removal of solvent from the residual solution and sublimation (120°) gave trimethyltin hydroxide, m.p. 118° (decomp.) (identified by i.r.).

(d) *With bromine.* Excess of bromine (3·1 g.) in benzene (20 ml.) was added dropwise to bis(trimethylstannyl)diazomethane (1·865 g.) in a flask attached *via* a trap (—196°) to a gas burette. A non-condensable gas (82·2 ml.) was evolved [$(Me_3Sn)_2CN_2$ requires N_2, 114 ml.]. Trimethyltin bromide (1·21 g., 49%) was distilled from the residue and identified by its i.r. spectrum and by analysis (Found: C, 14·6; H, 3·74. Calc. for C_3H_9BrSn: C, 14·8; H, 3·72%).

(e) *With phenylacetylene.* Phenylacetylene (3·0 g.) in benzene (10 ml.) was added to bis(trimethylstannyl)diazomethane (1·55 g.); the mixture was heated under reflux ($\frac{1}{2}$ hr.). Distillation yielded phenyl(trimethylstannyl)acetylene (1·32 g., 56%), b.p. 68°/0·3 mm., identified also by its i.r. and ^1H n.m.r. spectra.

(f) *With cyclopentadiene.* Freshly distilled cyclopentadiene (5 ml.) in ether (10 ml.) was added to bis(trimethylstannyl)diazomethane (3·10 g.); the mixture was heated under reflux (4 hr.). Distillation of the mixture gave, after removal of ether, cyclopentadienyltrimethylstannane (1·5 g., 38%), b.p. 30°/1 mm., identified also by its ^1H n.m.r. spectrum.

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