

## CHROMATOGRAPHIC STUDIES ON ORGANO-TIN COMPOUNDS

## PART II. THE REACTIONS OF TRIMETHYLSTANNANE

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Although considerable work has been published on organo-stannanes, it has mainly concerned the aromatic stannanes, *e.g.* triphenylstannane. A review of organotin chemistry was compiled by INGHAM, ROSENBERG AND GILMAN<sup>1</sup>, while further reviews by LUITJEN, VAN DER KERK AND NOLTES<sup>2,3</sup> and NEUMANN<sup>4</sup> have also been published.

This paper describes the preparation of trimethylstannane, and its reactions with organic halides, sulphides, amines, alcohols, olefins and acetylenes. The products of each reaction were identified and investigated by infra-red spectroscopy, gas-liquid chromatography, distillation and refractive index techniques:

## PREPARATION OF TRIMETHYLSTANNANE

Trimethylstannane was prepared by the normal three-stage synthesis:

(a) Reaction of stannic chloride with an excess of methyl magnesium iodide in diethyl ether, under the usual Grignard conditions. After refluxing, the resultant mixture was baked until all the volatile material had been collected. (The usual procedure of the addition of water, to destroy the excess Grignard reagent was not followed, since it was found to lower the yield of tetramethylstannane, and to produce a large quantity of unidentified higher boiling-point compounds.) The tetramethylstannane was fractionated from the mixture at 78°. The purity of the product was checked by gas chromatography.

(b) Trimethylbromostannane was then prepared from tetramethylstannane by addition of the stoichiometric concentration of bromine, and refluxing in diethyl ether. The bromo-compound was purified by distillation.

(c) Trimethylstannane was prepared by the method due to FINHOLT *et al.*<sup>5,6</sup> and VAN DER KERK *et al.*<sup>7</sup>. Trimethylbromostannane was added slowly to an excess of lithium aluminium hydride in di-*n*-butyl ether (in an atmosphere of nitrogen) at room temperature. After gentle refluxing, the stannane was distilled at 59° from the mixture, and stored under nitrogen.

## REACTIONS OF TRIMETHYLSTANNANE

The reactions of trimethylstannane were carried out using stoichiometric quantities of reagents, under an atmosphere of nitrogen. Usually, the mixtures were

gently refluxed to produce reaction, but in some cases, higher temperatures and pressures were employed by using sealed-glass tubes.

#### *Reaction with organic halides*

Trimethylstannane reacted exothermally with aliphatic bromides and aliphatic or aryl iodides, to produce the corresponding hydrocarbon and the trimethyl-halogenostannane:

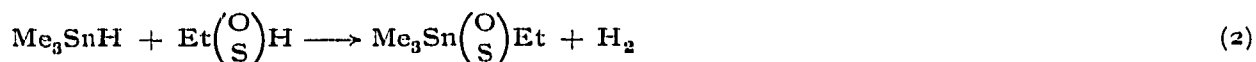


R = alkyl or aryl group; X = halogen

Chloro-compounds and aryl bromides, however, reacted only after prolonged refluxing, giving small yields of products. These experiments confirmed the observations of ROTHMAN AND BECKER<sup>8,9</sup> that the reactivity of the tin-hydrogen bond towards alkyl halides increases in the order  $\text{RCl} > \text{RBr} > \text{RI}$ . The reaction mechanism of such stannane reactions was first thought to be ionic<sup>10,11</sup>, the tin-hydrogen bond being polarised in the direction  $\text{Sn}^{\delta+} \longrightarrow \text{H}^{\delta-}$ ; and this has been used to explain the greater reactivity of alkyl iodides than alkyl chlorides. However, recent observations reported by KUIVILA, MENAPACE AND WARNER<sup>12</sup> indicate that the reactions of trimethylstannanes occur through a radical mechanism, the rate-determining step being the formation of radicals from the organic halides, and further evidence for this theory is the catalytic effect of azoisobutyronitrile on such reaction systems<sup>13</sup>. The addition of trimethylstannane to olefins also indicates a free radical mechanism.

#### *Reaction with alcohols, sulphides or amines*

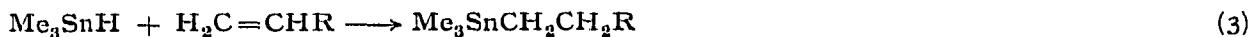
On refluxing alcohols or mercaptans with trimethylstannane, small amounts of the corresponding addition compounds are produced. Such compounds rapidly decompose in air, the reactions may be represented as follows:



However, in the case of disulphides, primary, secondary and tertiary amines, no reaction with trimethylstannane was observed, unlike the reaction of triphenylstannane with amines<sup>11, 14-17</sup>.

#### *Reaction with olefins*

Mixtures of trimethylstannane and olefins on refluxing give small yields of the corresponding addition compounds:



R = alkyl group

VAN DER KERK, NOLTES AND HENRY<sup>18,19</sup> suggested that the presence of a functional group or a conjugated double bond will facilitate the addition of unsaturated linkages to a tin-hydrogen bond. Such hydrostannation of olefins appears to proceed by a free radical mechanism<sup>13,20</sup>. It, therefore, seemed worthwhile to investi-

gate the behaviour of conjugated dienes in such a reaction. Piperylene (penta-1,3-diene) was readily available and it was decided to examine this reaction.

(a) *Piperylene*. Piperylene, together with other conjugated dienes<sup>21</sup>, is readily hydrostannated at 60–85° by a radical mechanism. NEUMANN AND SOMMER<sup>22</sup> have shown that radical scavengers inhibit, and radical producers, *e.g.* azoisobutyronitrile, accelerate the reaction. BARNETSON, CLARK AND KWON<sup>23</sup> suggest that for the addition of dimethylstannane to conjugated dienes, their evidence indicates that it is the stannane which plays the major role and that formation of radicals from the olefin is not the rate-determining step. Further work since the publication of COOKE, NICKLESS AND POLLARD<sup>24</sup> now confirms this viewpoint.

Chromatographic analyses of the reaction mixture indicated the presence of four reaction products, and a typical chromatogram is shown in Fig. 1. The assignment of peaks is as follows: a = unchanged piperylene; b = tetramethylstannane; c, d, e, f = monoaddition products.

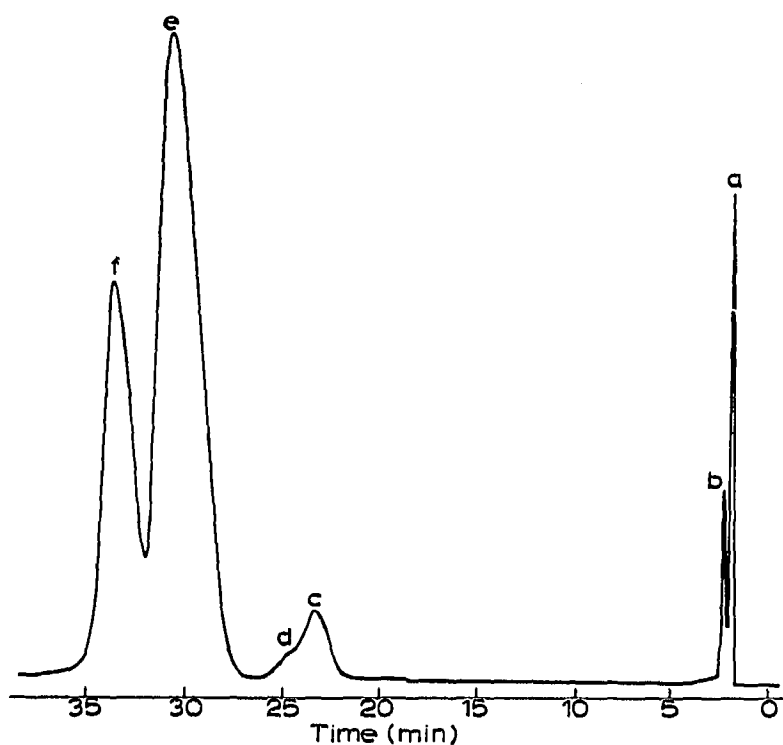


Fig. 1. Elution pattern for the trimethylstannane-piperylene reaction. a = piperylene; b = tetramethylstannane; c, d, e, f = monoaddition products.

If these pentenyl compounds are formed, it is probably by simple 1,4- and 1,2-addition (compare ref. 24, where only 1, 2-addition was considered) to the conjugated system of piperylene. The configuration about the C=C bond is of great interest, since the following *cis* and *trans* isomers are possible, assuming addition of  $-\text{SnMe}_3$  at the 1-carbon atom.

By considering the stereochemistry of the reaction, it was thought that addition of the  $-\text{SnMe}_3$  group at carbon numbers 3 and 4 would be almost impossible because of steric hindrance. Also examination of the two doublet elution peaks suggested the presence of two sets of *cis* and *trans* isomers which would be expected if



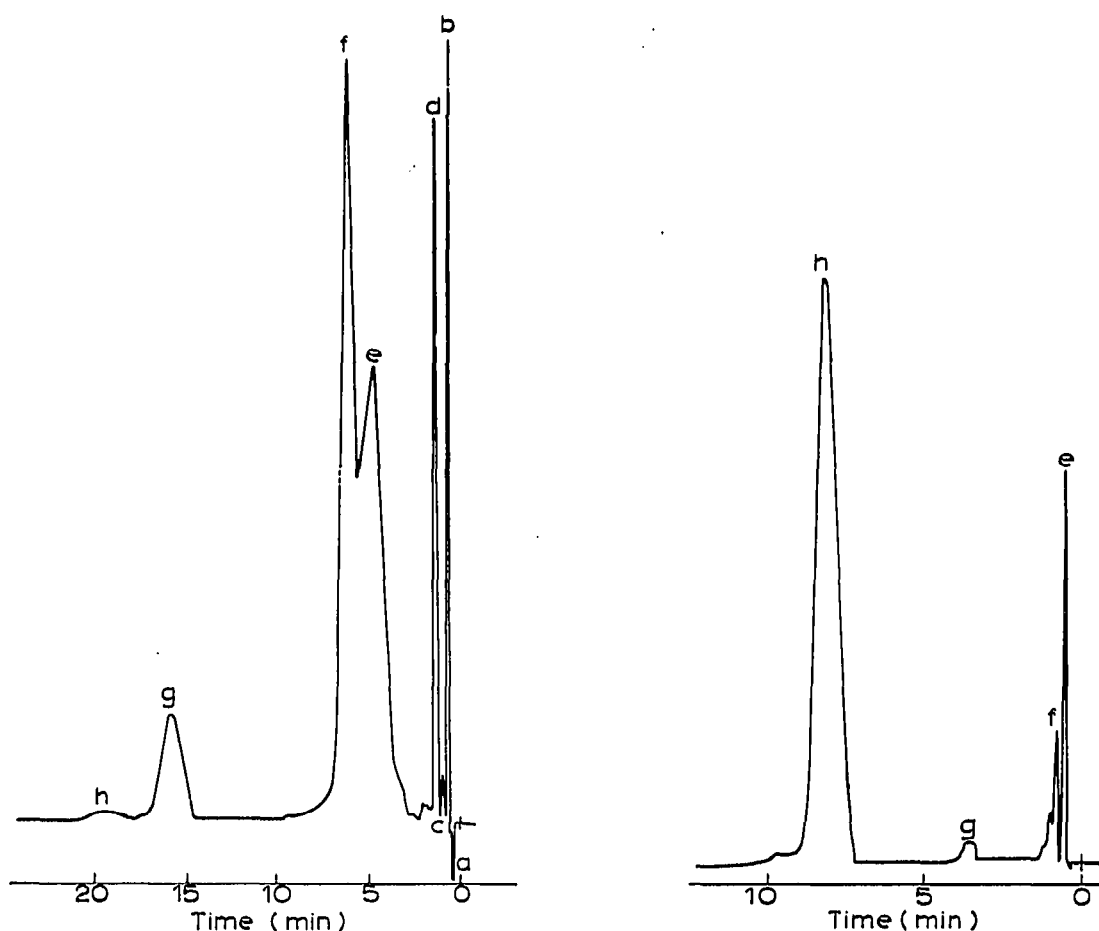


Fig. 2. Elution pattern for the trimethylstannane-pent-1-ene reaction (before decomposition). a = hydrogen; b = trimethylstannane; c = pent-1-ene; d = tetramethylstannane; e, f, h = unknown unstable compounds; g = trimethyl-*n*-amylstannane.

Fig. 3. Elution pattern for the trimethylstannane-pent-1-ene reaction (after decomposition). c = pent-1-ene; f = tetramethylstannane; g = di-*n*-butyl ether (solvent); h = trimethyl-*n*-amylstannane.

care was taken to exclude oxygen, and little tetramethylstannane was formed when trimethylstannane was heated alone. The unstable compounds were probably mixed organostannanes of the form  $\text{Me}_2\text{RSnH}$ , but although the tin-hydrogen bond reacts readily with oxygen, the decomposition of these reaction products was far more rapid than that of trimethylstannane. These unstable intermediates suggest that two mechanisms can operate in these hydrides with olefins, probably a free radical, which confirms the results of catalytic studies by NEUMANN, NIERMANN AND SOMMER<sup>13</sup> and FUCHS AND GILMAN<sup>27</sup>, and a four-centre mechanism. The former reaction is favoured by higher pressures; however, further work is needed to clarify this situation.

The identities of the stable trimethylalkylstannanes formed were confirmed by:

1. Comparing their retention volumes with those of authentic samples (prepared by Grignard synthesis) and plotting a graph of  $\log$  (specific retention volume) against carbon number of the chain (see Fig. 4).

2. Infra-red spectroscopy, and conventional analysis.

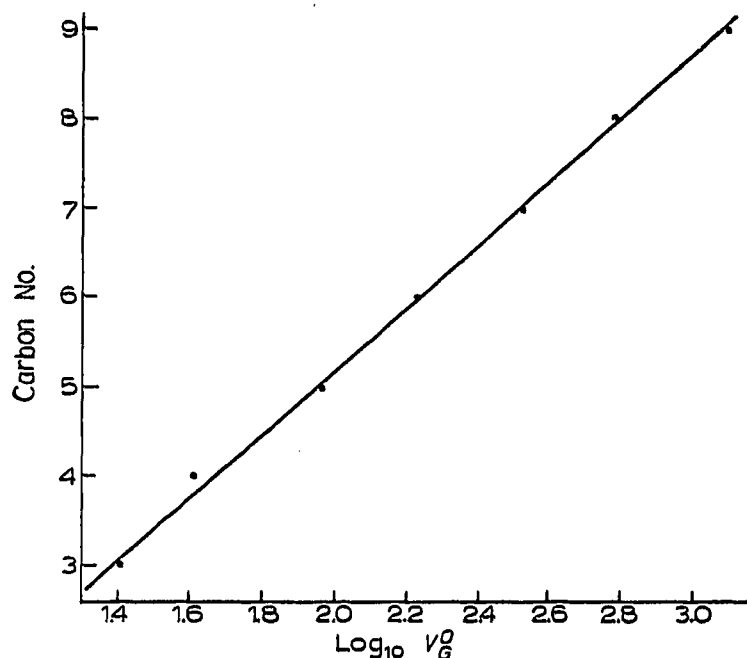


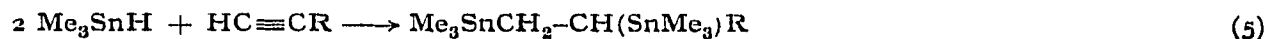
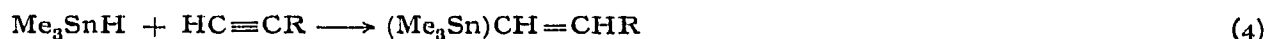
Fig. 4. Graph of log (specific retention volume) ( $\log_{10} V_G^0$ ) versus the number of carbon atoms in the molecule, for the trimethylalkylstannane series.

#### Reaction with acetylenes

VAN DER KERK AND NOLTES<sup>18</sup> found that organostannanes reacted far more readily with acetylenes than olefins, and this was certainly the case with trimethylstannane, the reaction being exothermic.

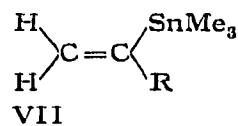
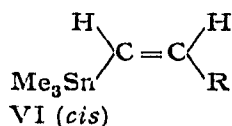
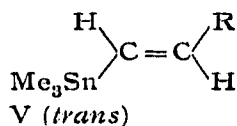
(a) *Monoacetylenes*. SMOLIN<sup>28</sup> studied the reaction of tri-*n*-butylstannane on acetylenes using azoisobutyronitrile as catalyst, indicating that free radicals entered into the addition reactions. By comparing the rates of reaction of trimethylstannane with olefins and acetylenes, the rate-determining step is probably the formation of radicals from the unsaturated hydrocarbons, since if the reaction was governed by formation of radicals from the stannane, the rates of reaction for the two series of compounds would be almost identical.

For a given triple bond, the mono- and di-addition compounds were formed, *viz.*



R = alkyl group.

The addition product formed in eqn. (4) may exist in any of the three forms below:



Chromatography of the monoaddition products formed in the first stoichiometric reaction showed that at least two components were formed, being present in the proportion of 15:1. The elution curve for the stannane-1-pentyne reaction is given in Fig. 5.

On considering the stereochemistry of the addition reaction, peak c in Fig. 5 is the product of addition at the 1-carbon atom, and is probably a mixture of V and VI. However, the *cis*-form VI would be expected to have the longer retention time, but it was impossible to resolve peak c into two peaks. Peak b must be due to structure VII; such reasoning was confirmed because for a given carbon chain, the closer towards the centre the trimethylstannane group is attached, the shorter the retention time. This was demonstrated in the series of compounds formed when trimethylstannane was added to 1-heptyne, 2-heptyne and 3-heptyne. The retention ratios of the three most stable isomers formed in these reactions over a silicone oil E-301 phase at 150° are given in Table I.

Fig. 6 shows the relationship between the log (specific retention volume) and the bonding position of the trimethylstannyl group, for the compounds in Table I. Fig. 7 shows the log (specific retention volume) and added carbon number relationship for the three series of compounds, *viz.*:

- (a) 2-alkyl-1-enyl-trimethylstannanes,  $H_2C=C(SnMe_3)R$ ;
- (b) 1-alkyl-1-enyl-trimethylstannanes,  $Me_3SnCH=CHR$ ;
- (c) 1,2-bis-(trimethylstannyl)-alkanes  $Me_3SnCH_2CH(SnMe_3)R$ .

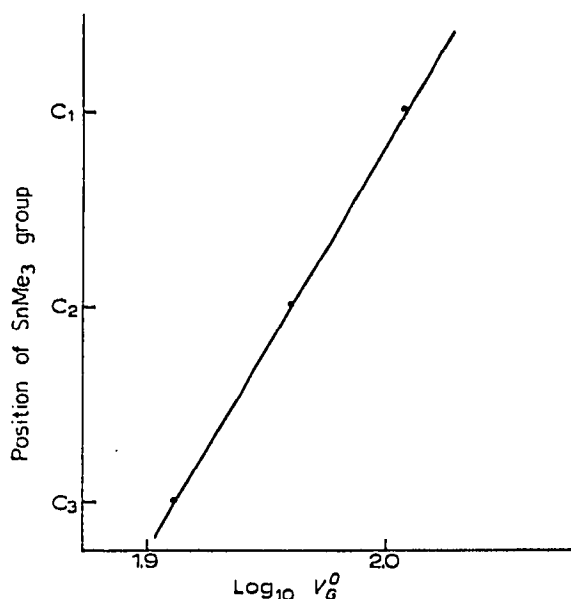
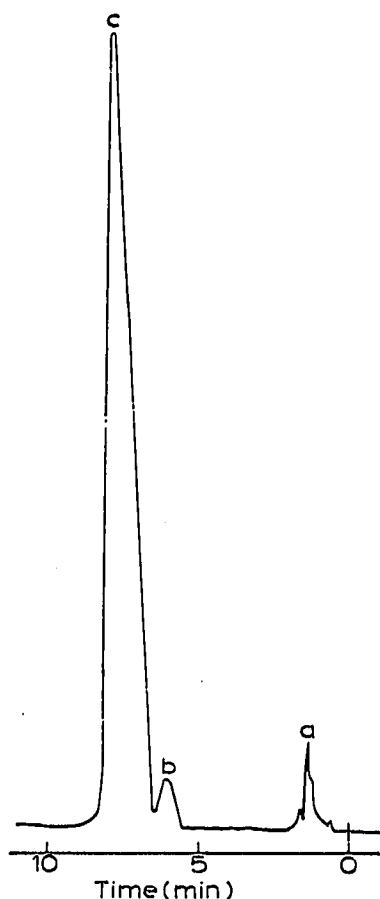


Fig. 5. Elution pattern for the trimethylstannane-1-pentyne reaction. a = tetramethylstannane; b = pent-1-enyl-(2-tin)-trimethylstannane; c = pent-1-enyl-(1-tin)-trimethylstannane.

Fig. 6. Graph of log (specific retention volume) ( $\log_{10} V_g^0$ ) versus the bonding position of the trimethylstannyl group.





TABLE II

INFRA-RED SPECTRA OF THE TRIMETHYLSTANNANE-ACETYLENE ADDITION COMPOUNDS

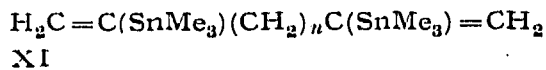
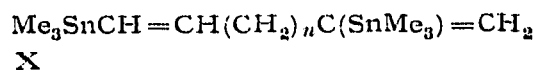
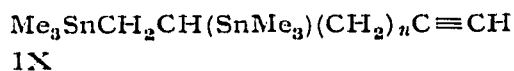
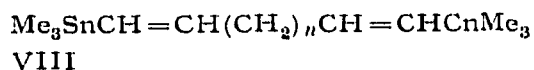
Compound	Absorption frequencies (cm <sup>-1</sup> )*								
	$\nu_s$ Sn- Me <sub>3</sub>	$\nu_{as}$ Sn- Me <sub>3</sub>	R Sn- Me <sub>3</sub>	$\delta_s$ CH <sub>3</sub>	$\nu_{as}$ CH <sub>3</sub>	$\delta_s$ C=C			
1-Pent-1-enyl-trimethylstannane		528	715	768	1192	1381	1437	1464	1600
2-Pent-2-enyl-trimethylstannane	512	526	709	768	1191	1373	1453		1624
1-Hept-1-enyl-trimethylstannane	513	528	717	768	1192	1381	1433	1468	1600
2-Hept-2-enyl-trimethylstannane		526	709	767	1190	1378	1468		1619
3-Hept-3-enyl-trimethylstannane	514	526	708	766	1190	1380	1464		1621
1-Oct-1-enyl-trimethylstannane		520	720	766	1190	1380	1437	1468	1600
4-Oct-4-enyl-trimethylstannane	513	525	709	768	1190	1379	1434	1467	1623
1-Non-1-enyl-trimethylstannane	510	527	717	764	1189	1379	1434	1466	1600
4-Non-4-enyl-trimethylstannane		522	703	758	1186	1373	1433	1459	1617
1,2-Bis-trimethylstannyl- <i>n</i> -hexane		522	710	762	1190	1381		1468	1602
1,7-Bis-trimethylstannyl-1,6-heptadiene		528	713	766	1190		1437		1600
1,9-Bis-trimethylstannyl-1,8-nonadiene		527	711	764	1183		1431	1461	1596

\*  $\nu$  = stretching frequency;  $\delta$  = deformation frequency; R = rocking frequency; s = symmetric; as = asymmetric.

1. Tin-hydrogen bond stretching frequency (1837 cm<sup>-1</sup> in trimethylstannane).
2. Olefinic carbon-carbon bond stretching frequency (1600 cm<sup>-1</sup>).
3. Acetylenic carbon-hydrogen bond stretching frequency (3250 cm<sup>-1</sup>).
4. Acetylenic carbon-carbon bond stretching frequency (2200-2350 cm<sup>-2</sup>).

This fact is demonstrated by the infra-red spectra of trimethylstannane, 1-heptyne and trimethyl-1-(hept-1-enyl)-stannane, which are shown in Fig. 8, respectively a, b and c.

(b) *Diacetylenes*. The reactions of trimethylstannane with two diacetylenes were also investigated, and found to be similar to the monoacetylene reactions. The reaction with 1,6-heptadiyne yielded one diaddition product only, but that with 1,8-nonadiyne gave rise to three compounds. One is a monoaddition product, the remaining two being diaddition products. Four possible structures of the diadducts are given below:



The structure which would be most readily formed is VIII, and the single reaction product of the heptadiyne addition product probably has this structure where  $n = 3$ . Infra-red analysis showed the presence of the double bond, the trimethylstannyl group, and the complete absence of acetylenic bonds. However, such evidence does not exclude structures X and XI, but since the addition to a 2-carbon atom is so low, it is thought that the assignment of structure VIII is correct.

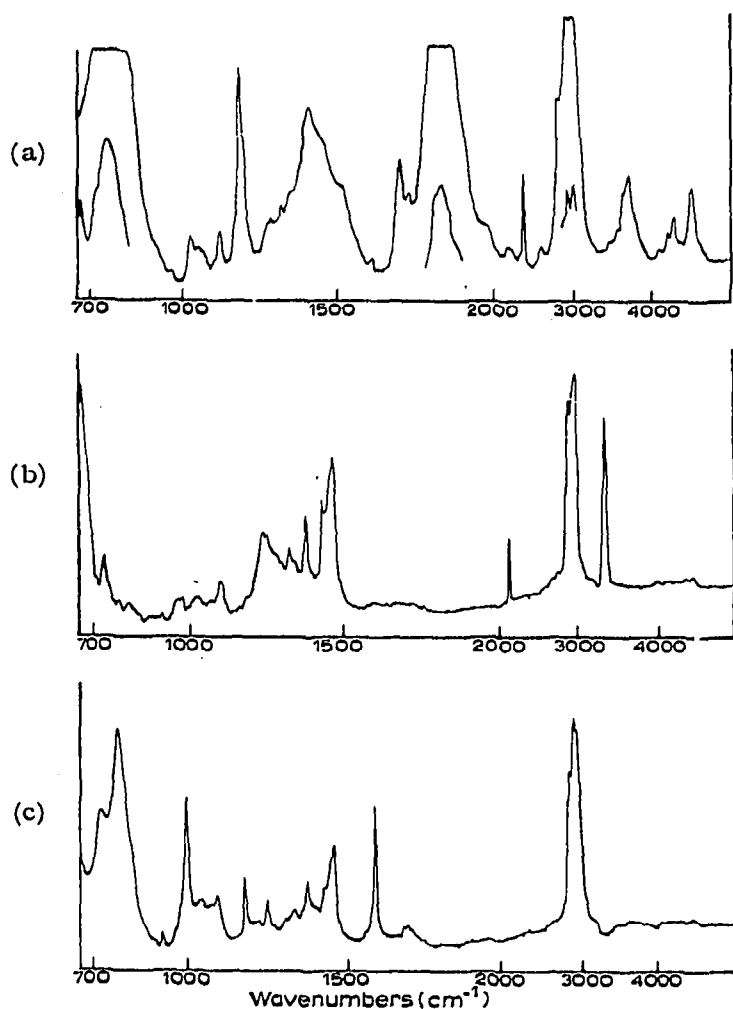
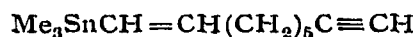
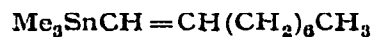


Fig. 8. Infra-red spectra of (a) trimethylstannane; (b) 1-heptyne; (c) trimethyl-1-(hept-1-enyl)-stannane.

The structure of the monoadduct formed with 1,8-nonadiyne is:



The amount of monoaddition product formed, however, was extremely small and could only be detected by gas-liquid chromatography where the initial peak on an elution diagram of the reaction had a retention time almost identical to the reaction product XII with 1-nonyne.



XII

The major diaddition product was identified as the compound of structure VIII where  $n = 5$ , because of infra-red spectra and the points discussed with reference to 1,6-heptadiyne. The secondary product, having a shorter retention volume and comprising 5% of the mixture, was assumed to be structure X where  $n = 5$ . The only

evidence for this assignment is the shorter retention time, and the relative probabilities of the formation of IX, X and XI, considering the steric hindrance involved in the three corresponding addition reactions.

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#### SUMMARY

Various types of organic compounds were refluxed with trimethylstannane, including halides, alcohols, mercaptans, amines, olefins and acetylenes. The products were fractionally distilled, and identified by gas chromatography, infra-red spectroscopy, etc.

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