THE REACTION OF HYDROGEN POLYSULFIDE WITH SELECTED OLEFINIC TIN COMPOUNDS

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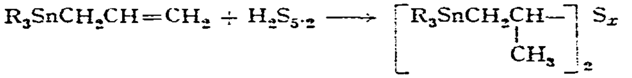
When diallyl- and di-β-methallylsilanes were treated with hydrogen polysulfide, low molecular weight polymers were obtained which contained both silicon and sulfur[1]. On this basis, it was hoped that the addition of hydrogen polysulfide to diallyl- and di-β-methallyltin compounds would produce tin containing polymers.

Initially, hydrogen polysulfide with the average composition $H_2S_{5.2}$ was added to a series of mono-olefinic tin compounds of the general formula R_3SnR', where R' is allyl or β-methallyl and R is ethyl, *n*-butyl, phenyl or *p*-tolyl. The reaction between allyltriphenyltin and hydrogen polysulfide at elevated temperatures resulted in the cleavage of the allyl group as well as one of the phenyl groups. Similarly, trimeric di-*p*-tolyltin sulfide was obtained from allyltri-*p*-tolyltin and hydrogen polysulfide under the same conditions.

$$(p\text{-}CH_3C_6H_4)_3SnCH_2CH{=}CH_2 \xrightarrow[150^\circ]{H_2S_{5.2}} [(p\text{-}CH_3C_6H_4)_2SnS]_3$$

When the monoallyltin compounds were treated with hydrogen polysulfide at room temperature, addition to the double bond rather than cleavage of groups was found to take place.



$$R_3SnCH_2CH{=}CH_2 + H_2S_{5.2} \longrightarrow \left[R_3SnCH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{—}\right]_2 S_x$$

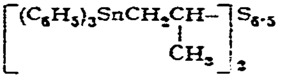
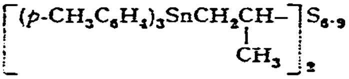
The polysulfides formed in this manner were assigned the structures listed in Table 1 on the basis of elemental analysis, average molecular weight and infrared data.

These compounds were unstable above room temperature and decomposed rapidly on heating to form bis(trialkyl) or bis(triaryltin) polysulfides and propylene. The sulfides resulting from the beta elimination of the hydrogen polysulfide adducts, while having a variable sulfur content, all contain less sulfur than the parent compounds.

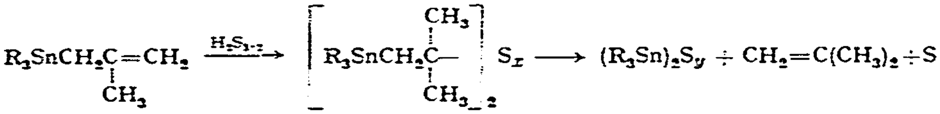
When comparing the infrared spectra of the polysulfides with those of the allylic starting materials, a noticeable increase in terminal methyl absorption at 1375 cm^{-1} was observed in the case of the ethyl and *n*-butyl compounds. The allyltriaryltin compounds have no band at 1375 cm^{-1} while their hydrogen polysulfide adducts exhibit a moderately strong absorption in this region. Decomposition results in a disappearance of this band in the aryl compounds and its diminution in the alkyl compounds.

TABLE I

THE HYDROGEN POLYSULFIDE ADDITION TO OLEFINIC TIN COMPOUNDS

Monomer	*Polysulfide isolated*	*Decomposition product*
$(C_2H_5)_3SnCH_2CH{=}CH_2$	 $\left[(C_2H_5)_3SnCH_2\underset{\substack{\vert\\CH_3}}{C}H-\right]_2S_{6\cdot0}$	$[(C_2H_5)_3Sn]_2S_{1\cdot3}$
$(n\text{-}C_4H_9)_3SnCH_2CH{=}CH_2$	 $\left[(n\text{-}C_4H_9)_3SnCH_2\underset{\substack{\vert\\CH_3}}{C}H-\right]_2S_{6\cdot6}$	$[(n\text{-}C_4H_9)_3Sn]_2S_{1\cdot3}$
$(C_6H_5)_3SnCH_2CH{=}CH_2$	 $\left[(C_6H_5)_3SnCH_2\underset{\substack{\vert\\CH_3}}{C}H-\right]_2S_{6\cdot5}$	$[(C_6H_5)_3Sn]_2S_4$
$(p\text{-}CH_3C_6H_4)_3SnCH_2CH{=}CH_2$	 $\left[(p\text{-}CH_3C_6H_4)_3SnCH_2\underset{\substack{\vert\\CH_3}}{C}H-\right]_2S_{6\cdot9}$	$[(p\text{-}CH_3C_6H_4)_3Sn]_2S$
$(C_2H_5)_2Sn(CH_2CH{=}CH_2)_2$	....	$[(C_2H_5)_2SnS_{1\cdot2}]_3$
$(n\text{-}C_4H_9)_2Sn(CH_2CH{=}CH_2)_2$	....	$[(n\text{-}C_4H_9)_2SnS_{1\cdot6}]_3$
$(C_2H_5)_3SnCH_2C(CH_3){=}CH_2$	....	$[(C_2H_5)_3Sn]_2S_{1\cdot4}$
$(n\text{-}C_4H_9)_3SnCH_2C(CH_3){=}CH_2$	....	$[(n\text{-}C_4H_9)_3Sn]_2S_{2\cdot3}$
$(C_6H_5)_3SnCH_2C(CH_3){=}CH_2$	....	$[(C_6H_5)_3Sn]_2S_3$
$(p\text{-}CH_3C_6H_4)_3SnCH_2C(CH_3){=}CH_2$	....	$[(p\text{-}CH_3C_6H_4)_3Sn]_2S$
$(n\text{-}C_4H_9)_2Sn(CH_2C(CH_3){=}CH_2)_2$	....	$[(n\text{-}C_4H_9)_2SnS_{1\cdot4}]_3$

The reaction of hydrogen polysulfide with the series of β-methallyltrialkyl- and -triaryltin compounds was found to proceed in much the same manner as above. The resulting products containing a *gem*-dimethyl group as well as a beta sulfur atom were found to be unstable at room temperature. Decomposition occurred on standing with the evolution of isobutylene and the formation of tin sulfides similar to those obtained from the allyl compounds.



$$R_3SnCH_2\underset{\substack{|\\CH_3}}{C}{=}CH_2 \xrightarrow{H_2S_{1\cdot x}} \left[R_3SnCH_2\overset{\substack{CH_3\\|}}{\underset{\substack{|\\CH_3}}{C}}-\right]_2 S_x \longrightarrow (R_3Sn)_2S_y + CH_2{=}C(CH_3)_2 + S$$

Infrared spectra of the adducts, obtained before decomposition showed a distinct doublet in the 1360–1385 cm^{-1} region, thus indicating the existence of a *gem*-dimethyl group. These bands disappeared after decomposition.

Diallyldiethyltin, diallyldi-*n*-butyltin and di-*n*-butyldi-β-methallyltin were found to undergo the same reactions with hydrogen polysulfide as did the corresponding monoallyl and -β-methallyl compounds. The infrared spectra of these reaction products showed the same characteristics as those above. Similarly, on purification, these polysulfides decomposed to give diethyltin sulfides and di-*n*-butyltin sulfides, respectively. Molecular weight determinations indicated these sulfides to be trimeric.

The instability of the hydrogen polysulfide adducts and the nature of the decomposition products together with significant changes in the infrared spectra during the course of reaction and decomposition indicate that the reaction proceeded to give Markownikoff addition in an ionic reaction.

INFRARED DATA

When an allyltin compound has reacted with hydrogen polysulfide, the absorption bands due to unsaturation at 3060, 1620, 985 and 880 cm^{-1} all disappear along with a weak band at 930 cm^{-1}. Apparently, this band is attributable to unsaturation, but it is not listed by Bellamy[2]. However, it is listed among the absorptions for allyltrimethyltin by Egorov[3].

In addition to increases in the methyl and methylene absorptions, new bands occur at 1230, 1120 and 1092 cm^{-1} throughout the series of allyl adducts. In all cases after heating and subsequent elimination of propylene, the three bands disappeared indicating that they are probably due to the propylene group.

The reaction of β-methallyltin compounds with hydrogen polysulfide resulted in the loss of five bands: the 3060, 1625 and 860 cm^{-1} absorptions as well as one of medium intensity at 1275 cm^{-1} and a weak band at 973 cm^{-1}. The latter two are presumably due to unsaturation although they are not listed as such by Bellamy[2].

As previously mentioned, the products obtained from the reaction of hydrogen polysulfide and the β-methallyltin compounds were unstable to the extent that they could not be isolated without decomposition. However, spectra in carbon tetrachloride solution were obtained during the course of reaction and in all cases new bands were found at 1218, 1165, 1090, and 1060 cm^{-1} in addition to the doublet at 1375 cm^{-1}. After decomposition these bands had disappeared.

The new bands are probably attributable to the isobutylene group formed during the reaction.

EXPERIMENTAL PART

Hydrogen polysulfide and allyltriethyltin

Allyltriethyltin (10 g, 0.0405 mole) in 30 cc of carbon tetrachloride was treated in a flask equipped with condenser, addition funnel and magnetic stirrer, with 4.0 g (0.024 mole) of hydrogen polysulfide in 30 cc of carbon tetrachloride, with continucus stirring. The reaction was slightly exothermic. After 17 h some sulfur precipitated and was filtered. Most of the carbon tetrachloride was then removed by heating under water suction. The yellow oil remaining was precipitated from carbon tetrachloride by the addition of methyl alcohol, repeatedly, until infrared analysis showed no trace of unsaturation. The product was kept at —25° for two months to precipitate sulfur, yielding $[(C_2H_5)_3SnCH_2CH(CH_3)S_3]_2$. (Found: C, 31.34; H, 5.74; S, 28.00; Sn, 34.35; mol. wt., 672. $C_{18}H_{42}Sn_2S_6$ calcd.: C, 31.41; H, 6.15; S, 27.95; Sn, 34.49%; mol. wt. 688.)

TABLE 2

INFRARED ABSORPTION DATA

Bis[β-(triethylstannyl)-α-methylethyl] polysulfide	*Bis[β-(tri-n-butylstannyl)-α-methylethyl] polysulfide*	*Bis[β-(triphenylstannyl)-α-methylethyl] polysulfide*	*Bis[β-(tri-p-tolylstannyl)-α-methylethyl] polysulfide*	*Bis(triethyltin) polysulfide*	*Bis(tri-n-butyltin) polysulfide*	*Bis(triphenyltin) polysulfide*	*Bis(tri-p-tolyltin) polysulfide*
2940 (s)	2950 (s)	3040 (m)	3040 (m)	2940 (s)	2940 (s)	3040 (m)	3040 (m)
2900 (s)	2900 (s)	3000 (m)	3000 (m)	2900 (s)	2900 (s)	1960 (w)	3000 (m)
2860 (s)	2850 (s)	2960 (sh)	2950 (m)	2880 (s)	2840 (s)	1875 (w)	2960 (m)
2800 (m)	1460 (s)	2900 (w)	2910 (m)	2555 (m)	1460 (s)	1805 (w)	2920 (m)
2700 (w)	1420 (w)	1960 (w)	2860 (m)	1463 (m)	1415 (w)	1630 (w)	2860 (m)
1450–60 (m, broad)	1375 (m)	1875 (w)	1900 (w)	1420 (w)	1375 (m)	1480 (m)	1900 (w)
1420 (w)	1355 (w)	1805 (w)	1800 (w)	1375 (m)	1355 (w)	1430 (s)	1795 (w)
1375 (m)	1338 (w)	1635 (w)	1635 (w)	1230 (w)	1340 (w)	1365 (w)	1633 (w)
1230 (m)	1290 (w)	1575 (w)	1595 (s)	1185 (m)	1290 (w)	1325 (m)	1593 (s)
1180 (m)	1250 (w)	1480 (s)	1495 (s)	1013 (s)	1250 (w)	1295 (m)	1493 (s)
1120 (w)	1230 (w)	1450 (m)	1450 (s)	958 (w)	1180 (w)	1255 (w)	1450 (s)
1095 (m)	1180 (m)	1428 (s)	1390 (s)	940 (sh)	1145 (w)	1185 (m)	1390 (s)
1020 (m)	1120 (w)	1375 (m)	1375 (m)	670 (s)	1070 (m)	1150 (w)	1308 (m)
960 (w)	1090 (w)	1330 (m)	1320 (m)		1045 (w)	1070 (s)	1260 (w)
940 (w)	1070 (m)	1300 (m)	1203 (m)		1020 (w)	1020 (s)	1210 (w)
825 (w)	1040 (w)	1258 (w)	1230 (m)		1000 (w)	995 (s)	1185 (s)
785 (w)	1000–20 (w, broad)	1230 (w)	1210 (w)		960 (w)	908 (w)	1110 (w)
715 (m)	960 (w)	1185 (m)	1190 (s)		875 (m)	725 (s)	1070 (s)
	860–75 (m, broad)	1155 (w)	1110 (w)		863 (sh)	693 (s)	1035 (w)
668 (s)	770 (w)	1125 (w)	1095 (m)		840 (w)		1015 (s)
	745 (w)	1092 (m)	1070 (s)		770 (w)		790 (s)
	715 (m)	1070 (s)	1038 (w)		745 (w)		700 (w)
	690 (m)	1020 (s)	1020 (s)		690 (m)		
	665 (m)	995 (s)	985 (w)		665 (m)		
		965 (w)	845 (w)				
		908 (w)	790 (s)				
		875 (w)	720 (m)				
		850 (w)	705 (w)				
		725 (s)					
		695 (s)					

Thermal decomposition of bis[β-(triethylstannyl)-α-methylethyl] polysulfide

This mixture of compounds ($x = 6.0$) was heated in a flask provided with condenser and stirrer and connected to a Dry Ice trap. The flask was immersed in a decalin bath at 165°. Heating was continued until foaming had ceased. The gas in the trap was identified as propylene by its infrared curve (Sadtler[*] spectrum No. 6403). Bromination yielded 1,2-dibromopropane (Sadler[*] spectrum No. 3649), b.p. 138° (lit.[5] 140°). The yellow oil in the flask was boiled with 95% ethyl alcohol to remove sulfur, then filtered. The clear yellow oil did not lose sulfur at the temperature of Dry Ice, nor did it solidify. The infrared curve of this product was identical with that of triethyltin chloride, but the analysis indicated that it was $[(C_2H_5)_3Sn]_2S_{1.3}$. (Found: C, 31.79; H, 6.49; S, 9.02; Sn, 51.81; mol. wt. 442. $C_{12}H_{30}Sn_2S_{1.3}$ calcd.: C, 31.72; H, 6.61; S, 9.25; Sn, 52.42%; mol. wt., 454.)

Hydrogen polysulfide and allyltri-n-butyltin

Similarly, 10 g (0.03 mole) of allyltri-*n*-butyltin reacted with 4.0 g (0.024 mole) of hydrogen polysulfide to form $[(n\text{-}C_4H_9)_3SnCH_2CH(CH_3)S_{3.3}]_2$. (Found: C, 40.77; H, 7.38; S, 24.35; Sn, 27.18; mol. wt., 873. $C_{30}H_{66}Sn_2S_{6.6}$ calcd.: C, 41.24; H, 7.62; S, 24.08; Sn, 27.17%; mol. wt., 889.)

Thermal decomposition of bis[β-(tri-n-butylstannyl)-α-methylethyl] polysulfide

In a manner similar to that used in the former pyrolysis, this mixture ($x = 6.6$) was heated producing propylene and $[(n\text{-}C_4H_9)_3Sn]_2S_{1.3}$. (Found: C, 46.60; H, 8.54; S, 6.90; Sn, 38.11; mol. wt., 697. $C_{24}H_{54}Sn_2S_{1.3}$ calcd.: C, 46.30; H, 8.68; S, 6.75; Sn, 38.26%; mol. wt., 622.)

Hydrogen polysulfide and allyltriphenyltin

A solution of allyltriphenyltin (5.0 g, 0.013 mole) in 25 cc of benzene was treated with 3.0 g (0.018 mole) of hydrogen polysulfide with stirring, heated on the steam bath until all of the benzene had evaporated, then heated in a wax bath at 150° for 2 h. All of the hydrogen sulfide had been driven off by this time, as indicated by the lead acetate test. After cooling, the solid reaction mixture was dissolved in chloroform and chilled in Dry Ice to remove dissolved sulfur. The solution was then filtered and the solute separated by the addition of methyl alcohol. The viscous oil was purified from traces of solvent by heating on a steam bath for 3 h. An infrared spectrum of this residue indicated complete absence of any aliphatic character. After standing for several weeks, the product slowly crystallized. It was taken up in a minimum amount of trichloroethylene and reprecipitated by the addition of a minimum amount of pentane, as a yellow crystalline solid. This process was repeated four times until the crystals were white. Infrared data confirmed its identity as trimeric diphenyltin sulfide, m.p. 182–3° (lit.[4] 183–4°).

When repeated, this reaction at room temperature yielded $[(C_6H_5)_3SnCH_2CH(CH_3)S_{3.25}]_2$. (Found: C, 50.55; H, 4.22; S, 21.75; Sn, 23.90; mol. wt., 994. $C_{42}H_{42}Sn_2S_{6.5}$ calcd.: C, 50.55; H, 4.21; S, 21.36; Sn, 23.87%; mol. wt., 997.)

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Thermal decomposition of bis[β-(triphenylstannyl)-α-methylethyl] polysulfide

Similarly, this mixture ($x = 6.5$) produced, on the application of heat, propylene and $[(C_6H_5)_3SnS_2]_2$, m.p. 118–25°. (Found: C, 51.82; H, 3.78; S, 15.61; Sn, 28.55; mol. wt., 780. $C_{36}H_3Sn_2S_4$ calcd.: C, 52.17; H, 3.62; S, 15.46; Sn, 28.74%; mol. wt., 828.)

Hydrogen polysulfide and allyltri-p-tolyltin

In a similar manner, 9.2 g (0.021 mole) of allyltri-*p*-tolyltin and 4.0 g (0.024 mole) of hydrogen polysulfide reacted at 150° to form trimeric di-*p*-tolyltin sulfide, m.p. 188–9°. (Found: C, 50.50; H, 4.35; S, 10.05; Sn, 35.87; mol. wt., 976. $C_{42}H_{42}Sn_3S_3$ calcd.: C, 50.45; H, 4.20; S, 9.61; Sn, 35.79%; mol. wt., 999.)

This experiment was repeated without the use of heat. Stirring was continued for 17 h after which the system was filtered from sulfur and the solvent removed under vacuum. The product was $[(p\text{-}CH_3C_6H_4)_3SnCH_2CH(CH_3)S_{3.45}]_2$. (Found: C, 52.43; H, 4.76; S, 19.92; Sn, 21.31; mol. wt., 989. $C_{48}H_{54}Sn_2S_{6.9}$ calcd.: C, 52.91; H, 5.00; S, 20.31; Sn, 21.79%; mol. wt., 1089.)

Thermal decomposition of bis[(β-tri-p-tolylstannyl)-α-methylethyl] polysulfide

This mixture ($x = 6.9$) yielded propylene and $[(p\text{-}CH_3C_6H_4)_3Sn]_2S$, m.p. 141–2°. (Found: C, 62.05; H, 5.36; S, 3.98. $C_{42}H_{42}Sn_2S$ calcd.: C, 61.76; H, 5.15; S, 3.92%.)

Hydrogen polysulfide and triethyl-β-methallyltin

The action of 2.42 g (0.015 mole) of hydrogen polysulfide on 4 g (0.015 mole) of triethyl-*β*-methallyltin formed isobutylene (Sadtler spectrum No. 7858), which was brominated to 1,2-dibromo-2-methylpropane[6] (Sadtler spectrum No. 9777). The main product was $[(C_2H_5)_3SnS_{0.7}]_2$, b.p. 78.6–79.5°/0.03 mm. (Found: C, 32.02; H, 6.69; S, 9.70; Sn, 51.47; mol. wt., 455. $C_{12}H_{30}Sn_2S_{1.4}$ calcd.: C, 31.51; H, 6.56; S, 9.80; Sn, 51.86%; mol. wt., 457.)

Hydrogen polysulfide and tri-n-butyl-β-methallyltin

This reaction using 10 g (0.029 mole) of tin compound and 3.5 g (0.021 mole) of hydrogen polysulfide gave isobutylene and $[(n\text{-}C_4H_9)_3SnS_{1.15}]_2$. (Found: C, 44.60; H, 8.24; S, 10.90; Sn, 36.10; mol. wt. 696. $C_{24}H_{54}Sn_2S_{2.3}$ calcd.: C, 44.04; H, 8.26; S, 11.31; Sn, 36.39%; mol. wt., 654.)

Hydrogen polysulfide and triphenyl-β-methallyltin

Hydrogen polysulfide (3.0 g, 0.018 mole) and 10 g (0.025 mole) of triphenyl-*β*-methallyltin interacted to form isobutylene and $[(C_6H_5)_3SnS_{1.5}]_2$, m.p. 127–33°. (Found: C, 54.70; H, 4.18; S, 12.23; Sn, 29.12; mol. wt., 839. $C_{36}H_3Sn_2S_3$ calcd.: C, 54.27; H, 3.77; S, 12.06; Sn, 29.12%; mol. wt., 796).

Hydrogen polysulfide and tri-p-tolyl-β-methallyltin

Hydrogen polysulfide (3.0 g, 0.018 mole) reacted with tri-*p*-tolyl-*β*-methallyltin to form isobutylene and $[(p\text{-}CH_3C_6H_4)_3Sn]_2S$, m.p. 141–2°. (Found: C, 60.94; H, 5.10 S, 4.31; Sn, 29.43. $C_{42}H_{42}Sn_2S$ calcd.: C, 61.76; H, 5.15; S, 3.92; Sn, 29.17%.)

Hydrogen polysulfide and triphenyltin chloride

By a method similar to the above, without heating, 10 g (0.026 mole) of triphenyltin chloride reacted with 4.3 g (0.026 mole) of hydrogen polysulfide to form bis(triphenyltin) sulfide, m.p. 144–6° (lit.[7] m.p. 145–6°). The infrared spectrum was identical with those listed in the literature[4].

Hydrogen polysulfide and diallyldi-n-butyltin

Similarly, 15.5 g (0.049 mole) of diallyldi-*n*-butyltin reacted with 9.0 g (0.055 mole) of hydrogen polysulfide. A non-distillable product was obtained $[(n\text{-}C_4H_9)_2SnS_{1.6}]_3$. (Found: C, 34.03; H, 6.07; S, 17.99; Sn, 41.32; mol. wt., 808. $C_{24}H_{54}Sn_3S_{4.8}$ calcd.: C, 33.80; H, 6.33; S, 17.96; Sn, 41.91 %; mol. wt., 852.)

Hydrogen polysulfide and di-n-butyldi-β-methallyltin

These compounds reacted to form $[(n\text{-}C_4H_9)_2SnS_{1.4}]_3$. (Found: C, 35.40; H, 6.27; S, 15.97; Sn, 42.27; mol. wt., 795. $C_{24}H_{54}Sn_3S_{4.2}$ calcd.: C, 34.53; H, 6.41; S, 16.19; Sn, 42.81 %; mol. wt., 834.)

Hydrogen polysulfide

Hydrogen polysulfide was prepared in accordance with the method of Mellor[8], using sodium tetrasulfide. Molecular weight determination indicated the average composition to be $H_2S_{5.2}$.

SUMMARY

A series of mono- and diallyl- and β-methallyltin compounds was treated with hydrogen polysulfide to form tin containing polysulfides. In each case, the course of the reaction was followed by infrared spectroscopy and the mode of addition determined.

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Short Communications

The preparation of organolithium compounds by the transmetalation reaction

IX*. Benzyllithium

Gilman and McNinch have described the preparation of benzyllithium by lithium metal cleavage of benzyl ethers[2] and have reviewed previous literature concerning the preparation of this reagent[2,3]. We felt that none of the available procedures for benzyllithium was wholly satisfactory and that a practical laboratory procedure for benzyl-

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* Part VIII: ref. 1.

J. Organometal. Chem., 2 (1964) 431–433