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SOME REACTIONS OF TRIS(TRIMETHYLSTANNYL)- AND TETRAKIS(TRIMETHYLSTANNYL)-METHANE

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Summary

With a variety of electrophilic reagents reaction occurs exclusively at the CH_3–Sn bonds of $[(CH_3)_3Sn]_4C$ and $[(CH_3)_3Sn]_3CH$. While the inner Sn–C bonds remain intact, methyl groups may be progressively cleaved off, one from each of the trimethylstannyl groups; in the case of bromine a second Me group may be cleaved from each of the $SnMe_2Br$ groups. The various products were identified by ^1H, ^{13}C and ^{119}Sn NMR spectroscopy.

Introduction

The two sites, i.e. CH_3–Sn and CH_2–Sn, in bis(trimethylstannyl)methane are subject to preferential attack by different electrophiles. Thus protolysis yields only tetramethylstannane and acetoxy- (or trifluoroacetoxy-)trimethylstannane as initial product [1], whereas mercuric chloride, methyl mercuric chloride, and chlorotrimethylplumbane [1] and dichlorodimethylstannane and stannic chloride [2] exclusively cleave one or more CH_3–Sn bonds. On the other hand brominolysis and iodinolysis give mixed products arising from attack at both sites and the ratio of the products varies with the solvent employed. Thus $Br_2/CHCl_3$ and I_2/C_6H_5Cl each give 13% Sn–CH_2 cleavage and 87% Sn–CH_3 cleavage [1]. It is of some interest therefore to discover the preferred site for reaction in more crowded trimethylstannyl derivatives of methane.

The low temperature brominolysis of tetrakis(trimethylstannyl)methane (**1**) has been investigated briefly by Kuivila and DiStefano [3], who noted that the ^1H NMR spectrum of the product shows eight signals in the region 0.9 to 1.13 ppm, in addition to a strong signal for bromomethane (2.61 ppm). A weak signal assigned to $[(CH_3)_3Sn]_3CBr$ (0.09 ppm) and signal for bromotrimethylstannane (0.71 ppm ^2J(H,Sn) 61.5 Hz) were taken to indicate cleavage at both CH_3–Sn and C–Sn sites with the former predominating. With bromine, iodine or stannic chloride it is possible to displace one or, with considerable more difficulty, two of the CH_3–Sn

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groups in $(CH_3)_3SnC[Si(CH_3)_3]_3$, although under very severe conditions more generalised cleavages may occur [4].

Experimental

Most of the reactions studied were carried in NMR tubes and studied by observation of the ^1H, ^{13}C or ^{119}Sn NMR spectra. Except for iodinolysis in chlorobenzene, the solvent was deuterochloroform. To reduce the complexity of the spectral region studied, the primary references tetramethylsilane and tetramethylstannane were not usually added to reaction mixtures. Sometimes a cyclohexane reference was employed but frequently resonances were referenced to an already known resonance of the substrate or a product.

^1H NMR spectra were recorded at 100 MHz on either a JEOL MH-100 or PS-100 spectrometers. ^{13}C NMR spectra were obtained using a JEOL FX-100 instrument (2.35 T) at 25 MHz with an observation bandwidth of 4 KHz. The centre of the $CDCl_3$ triplet at 77.00 ppm provided the reference in most cases. ^{119}Sn NMR spectra were obtained at 37.08 MHz on the FX-100 instrument with bandwidths of 8 or 10 kHz. Chemical shifts calculated from the difference between the absolute frequencies for the sample and for tetramethylstannane agreed closely with values obtained with the internal reference.

Mass spectra were recorded by Mr. G.A. Macfarlane on a MS 902S instrument at 70 eV with an accelerating voltage of 8 kV.

Tetrakis(trimethylstannyl) methane (1)

Prepared by the reaction of carbon tetrachloride with trimethylstannyllithium in dry tetrahydrofuran, essentially as previously described [5], the crude product was sublimed at 140°C/50 mmHg and the first sublimate containing most of the residual by-products was rejected. Pure product, m.p. > 210°C, was obtained after several sublimations, and was characterized by mass spectrometry [5] and NMR spectroscopy. ^1H NMR (δ(ppm), $CDCl_3$) 0.15. (^2J(H,Sn) 50.7; 48.4 Hz), cf. 0.16 (^2J(H,Sn) 50.0; 48.0 Hz) (CCl_4) [5]. ^{13}C NMR ($CDCl_3$) $\delta(CH_3)$ −3.7 (^1J(C,Sn) 316.4; 302.7 Hz; ^3J(C,Sn) 11.7 Hz), cf. −3.4 (^1J(C,Sn) 318 Hz; ^3J(C,Sn) 11 Hz) (C_6D_6) [6]; δ(C) −25.9 cf. −26.7 (^1J(C,Sn) 107 Hz) (C_6D_6) [6]. ^{119}Sn NMR ($CDCl_3$) 49.7 (^2J(Sn,Sn) 310.5 Hz) cf. 49.8 (^2J(Sn,Sn) 325 Hz) (C_6D_6) [6].

Tris(trimethylstannyl)methane (8)

Prepared by the reaction of chloroform with trimethylstannyllithium in dry tetrahydrofuran, cf. [5], or by the careful addition of bromoform in dry tetrahydrofuran to the Grignard reagent from chlorotrimethylstannane and magnesium turnings, the crude product contained substantial quantities of bis(trimethylstannyl)methane amongst other by-products (as judged by ^1H NMR) as well as the required **8**. Distillation at < 0.8 mmHg gave a product, m.p. 38–39°C, which solidified in the collector. Purification by crystallization from ethanol gave white crystals, m.p. 48–49°C (cf. 47.5–48°C [5]). ^1H NMR (δ(ppm), $CDCl_3$) $\delta(CH_3)$ 0.10 (^2J(H,Sn) 51.0; 48.8 Hz); cf. $\delta(CH_3)$ 0.10 (^2J(H,Sn) 53.0; 50.5 Hz) and δ(CH) −0.72 (^2J(H,Sn) 65.0; 62.0 Hz) (CCl_4) [5].

Tetrakis[bromodimethylstannyl]methane (5a)

Bromine (0.48 g, 3.0 m*M*) was added to tetrakis(trimethylstannyl)methane (**1**) (0.50 g, 0.75 m*M*) in chloroform (2 ml) and the mixture was stirred at room temperature for 20 h. The solvent and the bromomethane product were removed by evaporation and the solid residue sublimed was at 190°C/0.5 mmHg to yield **5a** (0.56 g, 80%) with m.p. > 240°C. ^{1}H NMR ($CDCl_3$) 1.11 ppm (^2J(H,Sn) 58.4, 55.9 Hz). ^{13}C NMR ($CDCl_3$) $\delta(CH_3)$ 5.86 ppm (^1J(C,Sn) 393.6, 376.5 Hz); δ(C) 14.03 ppm (^1J(C,Sn) 87.2, 83.4 Hz). MS highest cluster at m/z 913 corresponding to $M^+ - 15$ with the isotopic pattern of Sn_4Br_4.

Tris[iododimethylstannyl]trimethylstannylmethane (4b)

A solution of tetrakis(trimethylstannyl)methane (**1**) (0.27 g, 0.4 m*M*) and iodine (0.31 g, 1.22 m*M*) in chloroform (2 ml) was stirred at room temperature for 24 h. Volatile materials were removed under light suction, warming being required for the last traces of excess iodine. Sublimation at 190°C/1 mmHg yielded **4b** (0.25 g, 62%) containing (by ^{1}H NMR) traces of the tetra- and di-iodo derivatives (**3b** and **5b**) which survived repeated sublimation. ^{1}H NMR ($CDCl_3$) 1.13 ppm (^2J(H,Sn) 56.3, 53.9 Hz) (18H); 0.49 ppm (^2J(H,Sn) 50.6, 48.4 Hz) (9H). ^{13}C NMR ($CDCl_3$) $\delta(CH_3)$ 6.91 ppm (^1J(C,Sn) 373.7, 357.4 Hz); $\delta(CH_3)$ −2.87 ppm (^1J(C,Sn) 336.7, 322.1 Hz). MS highest cluster at $m/z = 989$ corresponding to $M^+ - 15$ with the isotopic pattern of Sn_4I_3.

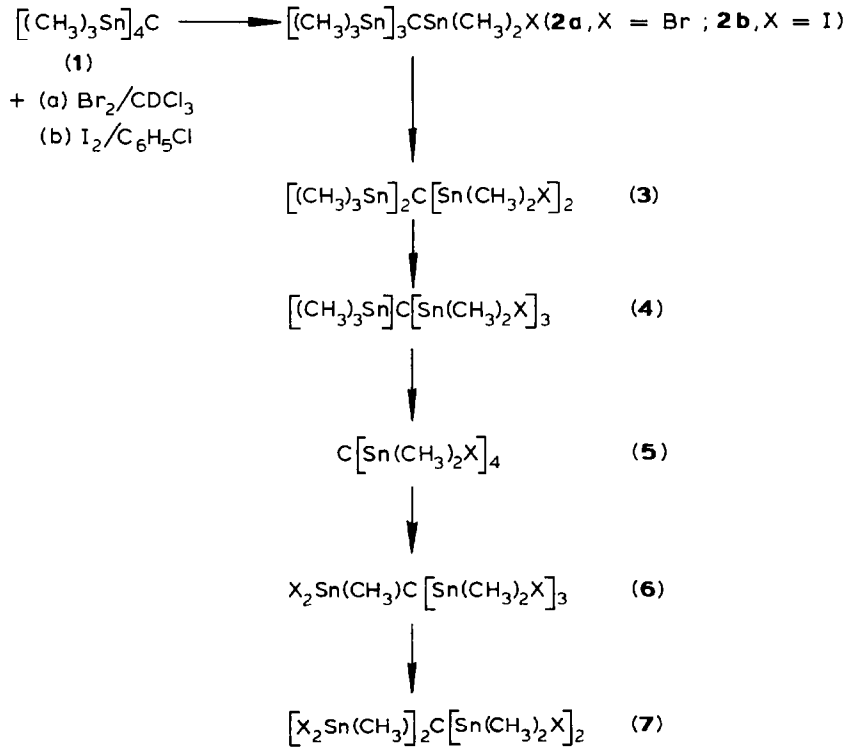
Tris[bromodimethylstannyl]methane (11)

Bromine (0.22 g, 1.38 m*M*) was added to tris(trimethylstannyl)methane (**8**) (0.23 g, 0.46 m*M*) in chloroform (2 ml) and the mixture was stirred at room temperature for 24 h. The solvent and the bromomethane product were removed by evaporation and the residue was heated at 65°C/0.1 mmHg for 4 h. Crystallisation of the resultant solid from dry ethanol gave colourless crystals of **11** m.p. 120–122°C (0.11 g, 34%). ^{1}H NMR ($CDCl_3$) $\delta(CH_3)$ 1.61 ppm (^2J(H,Sn) 61.3, 58.6 Hz) (18H); δ(CH) 2.15 ppm (^2J(H,Sn) 70.9, 67.8 Hz) (1H). ^{13}C NMR ($CDCl_3$) $\delta(CH_3)$ 3.81 ppm (^1J(C,Sn) 405.3, 387.7 Hz); δ(CH) 11.84 ppm (^1J(C,Sn) 190.4, 182.1 Hz). MS highest cluster at $m/z = 685$ corresponding to $M^+ - 15$ with the isotope pattern of Sn_3Br_3.

Results and discussion

Brominolysis of tetrakis(trimethylstannyl)methane

When tetrakis(trimethylstannane)methane (**1**) is treated with less than one equivalent of bromine in deuterochloroform solution the monobromo derivative **2a** is formed by exclusive Sn–CH_3 bond cleavage, but further reaction occurs. Thus with 0.7 equivalents of bromine a product containing **3a** (12%) and unreacted **1** (42%) as well as **2a** (46%) is obtained indicating that the reactivity of **2a** towards bromine is certainly not less than that of **1**. With further additions of bromine the reaction progresses as shown in Scheme 1. At all stages up to the formation of **5a** the reaction mixture consists of at least three compounds, i.e. **1**, **2a** and **3a** or **2a**, **3a** and **4a**, and selective formation of any one of these products is not possible. The formation of **5a** and especially its subsequent reactions are much slower, requiring a considerable excess of reagent, so that syntheses of **5a**, **6a** and **7a** are viable by this route. Details for **5a** are given in the experimental section.



SCHEME 1

These individual species were characterised by NMR spectroscopy on mixtures at various times in this progressive reaction. Details of the spectra are given in Table 1.

Small but characteristic trends in the ^1H chemical shifts and coupling constants are found to be essentially in accord with expectation based upon simpler compounds of this type [7]. The complex ^1H NMR spectrum previously reported [3] for this reaction is now explicable, but the reported presence of bromotrimethylstannane is not. We have found that without rigorous purification of tetrakis(trimethylstannyl)methane there are present impurities which on brominolysis yield bromotrimethylstannane and subsequently dibromodimethylstannane. There is otherwise no evidence for these as products, until the progressive brominolysis has reached the stage of **6a** → **7a** when a small amount of dibromodimethylstannane is found (^1H NMR spectrum only). Most reasonably this product arises from the cleavage of a C–Sn$(CH_3)_2$Br bond of **5a**, **6a** or **7a**, but no resonances that could be associated with the other product of such cleavage could be found, although expected to be rather more obvious. Unfortunately, these might have been obscured by the cyclohexane reference.

In the sequence **1** → **5a** there is a small progressive shift to low field for the ^{13}C chemical shifts of the $(CH_3)_3$Sn and the Br$(CH_3)_2$Sn groups as further bromines are introduced elsewhere in the molecule. There is perhaps also a progressive increase in $^1J(^{13}C;\ ^{119}Sn)$ although the low concentration of some species does not allow this coupling to be described. However the anomalous behaviour of **4a** indicates that this view of the chemical shifts is an oversimplification. The central (quaternary) carbons

TABLE 1

NMR DATA FOR TETRAKIS(TRIMETHYLSTANNYL)METHANE AND ITS BROMO DERIVATIVES

	1	2a	3a	4a	5a	6a	7a	cf.
^1H NMR [a]								
$\delta((CH_3)_3Sn)$	0.15	0.25	0.34	0.51	–	–	–	0.08 [c]
$^2J(^1H; ^{119}Sn)$	(50.7)	(51.6)	(?)	(53.6)				(51.6)
$\delta((CH_3)_2SnBr)$	–	0.71	0.85	1.02	1.11	1.18	1.27	0.74 [c]
$^2J(^1H; ^{119}Sn)$	–	(?)	(55.0)	(55.8)	(58.4)	(60.1)	(60.4)	(54.9)
$\delta((CH_3)SnBr_2)$	–	–	–	–	–	1.63	1.75	1.35 [e]
$^2J(^1H; ^{119}Sn)$						(68.2)	(70.4)	(68.0)
^{13}C NMR [a]								cf.
$\delta((CH_3)_3Sn)$	−3.71	−3.54	−3.26	−3.61	–			−9.6 [c]
$^1J(^{13}C; ^{119}Sn)$	(316.4)	(?)	(336.4)	(336.9)				(340)
$\delta((CH_3)_2SnBr)$	–	4.24	4.71	6.06	5.86			0.1 [d]
$^1J(^{13}C; ^{119}Sn)$		(?)	(?)	(391.6)	(393.7)			(372)
^{119}Sn NMR [a,b]								cf.
$\delta((CH_3)_3Sn)$	49.7	47.3	45.4	48.8	–	–		23.0 [f]
								(286)
$^2J(Sn–Sn)$	(324.8)*	(288.1)*	(255.3)*					41.0 [g]
								(309)
$\delta((CH_3)_2SnBr)$	–	164.6	151.7	124.3	116.5	107.9		136.2 [d]
$^2J(Sn'–Sn')$			(?)*	(234.9)*	(297.3)*	(261.7)*		
$^2J(Sn–Sn')$		334.0	315.4	339.4				
				363.3				
$\delta((CH_3)SnBr_2)$		–	–	–	–	29.7		68.4 [e]
$^2J(Sn'–Sn')$						360.1		

[a] $CDCl_3$ solutions. Chemical shifts in ppm (positive to low field) relative to $(CH_3)_4Si$ (for ^1H and ^{13}C) or $(CH_3)_4Sn$ (for ^{119}Sn); coupling constants in Hz. [b] $^{119}Sn–^{119}Sn$ coupling between equivalent (Sn–Sn or Sn'–Sn') sites calculated from observed $^{119}Sn–^{117}Sn$ coupling marked *. [c] $(CH_3)_4Sn$. [d] $(CH_3)_3SnBr$. [e] $(CH_3)_2SnBr_2$. [f] $[(CH_3)_3Sn]_2CH_2$ [7]. [g] $[(CH_3)_3Sn]_3CH$ [6].

could not be unambiguously identified. A similar anomaly for **4a** is evident for the trend to higher field in the ^{119}Sn chemical shifts of the $(CH_3)_3Sn$ groups in the sequence **1** → **4a**, although the larger response of the $Br(CH_3)_2Sn$ group for **2a** → **6a** appears to be more orderly.

A variety of satellites arising from $^2J(Sn–Sn)$ couplings can be observed in most of the ^{119}Sn spectra depending upon the composition of mixture under examination. Between equivalent tin atoms only the $^{119}Sn–^{117}Sn$ coupling can be seen, but between non-equivalent tin atoms both $^{119}Sn–^{119}Sn$ and $^{119}Sn–^{117}Sn$ couplings are visible. Detailed consideration of the appearance and intensities of these satellite patterns provides an identification of the species responsible, and confirms the analyses of the mixtures based upon their ^1H and ^{13}C spectra.

Iodinolysis of tetrakis(trimethylstannyl)methane

In chlorobenzene solution the exclusive and progressive cleavage of $Sn–CH_3$ bonds by iodine can be observed in a manner similar to that described above for brominolysis, except that because of the lower activity of the reagent reaction stops

TABLE 2

^{1}H NMR DATA FOR TETRAKIS(TRIMETHYLSTANNYL)METHANE AND ITS IODO DERIVATIVES [a]

	1	2b	3b	4b	5b	cf.
$\delta((CH_3)_3Sn)$	0.19	0.26	0.34	0.49	–	0.08 [b]
$^2J(^1H; ^{119}Sn)$	46.6	(49.4)	(50.1)	(50.6)		(51.4)
$\delta((CH_3)_2SnI)$	–	0.80	0.92	1.13	1.20	0.64 [c]
$^2J(^1H; ^{119}Sn)$		(49.8)	(52.7)	(56.3)	(56.9)	(54.6)

[a] C_6H_5Cl solutions. Chemical shifts in ppm relative to $(CH_3)_4Si$ (positive to low field); Coupling constants in Hz. [b] $(CH_3)_4Sn$ in C_6H_5Cl. [c] $(CH_3)_3SnI$ in C_6H_5Cl.

TABLE 3

^{1}H NMR DATA FOR TRIS(TRIMETHYLSTANNYL)METHANE AND ITS BROMO DERIVATIVES [a]

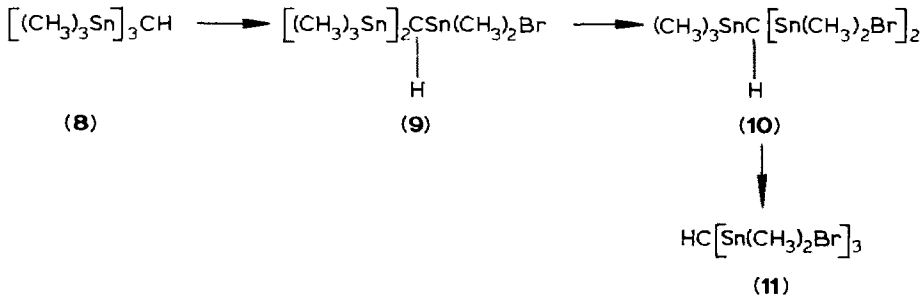
	8	9	10	11
$\delta((CH_3)_3Sn)$	0.10	0.20	0.28	–
$^2J(^1H; ^{119}Sn)$	(51.0)	(51.9)	(?)	
$\delta((CH_3)_2SnBr)$	–	0.69	0.83	1.01
$^2J(^1H; ^{119}Sn)$		(52.8)	(55.4)	(61.3)

[a] $CDCl_3$ solutions. Chemical shifts in ppm relative to $(CH_3)_4Si$ (positive to low field); Coupling constants in Hz.

at the stage of **5b**. Furthermore, conversion of **4b** to **5b** proceeds quite slowly (see Scheme 1) and **4b** (see Experimental) can be prepared. Once again only mixtures containing **1b**, **2b**, **3b** can be obtained. The ^{1}H NMR characteristics of the iodo derivatives are given in Table 2, where the trends noted for the bromo derivatives are again evident, but, unlike **4a**, without anomaly at **4b**.

Brominolysis of tris(trimethylstannyl)methane

Reaction of this species (**8**) with bromine in $CDCl_3$ solution also occurs only at the CH_3–Sn bonds (see ^{1}H NMR data in Table 3) until three of these have reacted as follows:

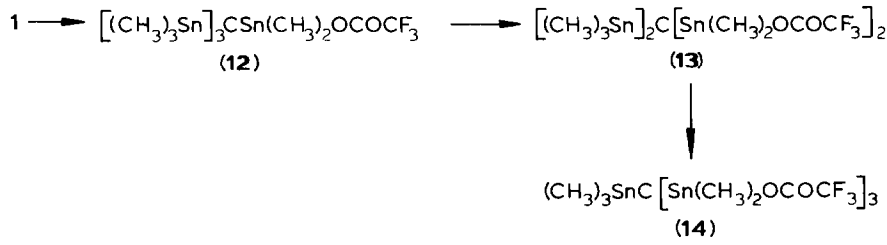


Further reaction of **11**, which can be isolated (see Experimental), with a large excess of bromine converts this product slowly to bromoform and dibromomethylstannane, a result confirmed in the ^{1}H NMR spectrum by the addition of authentic samples of these products. None of the intermediates arising from cleavage of the

central C–Sn bond, i.e. $[Br(CH_3)_2Sn]_2CHBr$ and $Br(CH_3)_2SnCHBr_2$, were detected, so that it seems that once this mode of cleavage sets in the remaining C–Sn bonds react rapidly. The lack of reactivity towards bromine at the central bonds of the series **1–5a**, of **8–10** and the low reactivity of **11** is clearly steric in origin, and as soon as this problem has been circumvented rapid cleavage ensues.

Trifluoroacetolysis to tetrakis(trimethylstannyl)methane

Although protolysis, with acetic acid or trifluoroacetic acid, of $(CH_3)_3SnCH_2Sn(CH_3)_3$ results in cleavage of the $Sn–CH_2$ bond only [1], the central Sn–C bonds are not the sites of reaction for **1**. With trifluoroacetic acid in $CDCl_3$ solution mixtures of the mono (**12**) and bis-trifluoroacetoxy (**13**) derivatives are obtained, and ultimately with excess acid the product is entirely **14**.



No further reaction occurs after long contact times with excess acid at room temperature (see Table 4 for ^1H NMR results).

Reaction of tetrakis(trimethylstannyl)methane with stannic chloride

With excess of anhydrous stannic chloride in $CDCl_3$ solution the reaction of **1** was almost instantaneous, yielding trichloromethylstannane and the tetrachloro derivative (**18**) together with a little of the trichloro derivative (**17**). Further additions of **1** yielded mixtures containing also the mono and dichloro derivatives (**15** and **16** respectively). These species were identified by their ^1H NMR spectra summarized in Table 4.

Acknowledgements

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TABLE 4

^1H NMR DATA FOR TRIFLUOROACETOXY AND CHLORO DERIVATIVES OF **1** [a]

	X = $OCOCF_3$			X = Cl			
	12	**13**	**14**	**15**	**16**	**17**	**18**
$\delta((CH_3)_3Sn)$	0.23	0.30	0.32	0.23	0.32	0.47	–
$^2J(^1H; ^{119}Sn)$	(50.2)	(51.0)	(?)	(?)	(?)	(51.2)	
$\delta((CH_3)_3SnX)$ [b]	0.74	0.79	0.82	0.61	0.75	0.87	0.96
$^2J(^1H; ^{119}Sn)$	(51.4)	(56.6)	(64.8)	(?)	(?)	(59.2)	(59.7)

[a] $CDCl_3$ solutions. Chemical shifts in ppm relative to $(CH_3)_4Si$ (positive to low field); Coupling constants in Hz. [b] cf. 0.70 (56.1) for $(CH_3)_3SnOCOCF_3$ and 0.65 (55.8) for $(CH_3)_3SnCl$.

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