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Diorganostannylenes. II. Photolytic Reaction of Diphenyltin with Alkyl Halides

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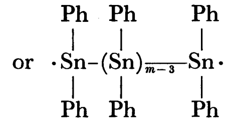
Synopsis. Photolysis of diphenyltin polymer, $(Ph_2Sn)_m$, afforded diphenylstannylene, Ph_2Sn:, which was captured by alkyl halides, R′X, to give the insertion products, $Ph_2R'SnX$. The reactivity of Ph_2Sn: was found to be lower than that of dibutylstannylene, Bu_2Sn:.

In continuation of our investigations of diorganostannylenes,[1-3] the photolytic formation and some reactions of diphenylstannylene have been investigated. Diphenylstannylene, transiently formed, has been efficiently captured by several alkyl bromides and methyl iodide.

A solution of pale yellow diphenyltin, $(Ph_2Sn)_m$,[4] in a large excess of ethyl bromide was irradiated with a high pressure mercury lamp through a pyrex filter at 0 °C to give a mixture of distillable phenyltin bromides: *viz.*, $Ph_2EtSnBr$ (64%), Ph_2SnBr_2 (20%), $PhEtSnBr_2$ (3%), and Ph_3SnBr (2%), together with a trace of undistillable stannoxanes. The major product, $Ph_2EtSnBr$, should be produced by the insertion reaction of diphenyl stannylene, Ph_2Sn: (**2**), into the C–Br bond of ethyl bromide (Eq. 2). The minor disproportionation products, Ph_3SnBr and $PhEtSnBr_2$, could be formed by the photo-induced transposition[1] of the phenyl group and the scrambling of the phenyl and bromide groups, respectively.

$$\underset{\mathbf{1}}{(Ph_2Sn)_m} \xrightarrow{h\nu} \underset{\mathbf{2}}{[Ph_2Sn:]} + \underset{\mathbf{1}}{(Ph_2Sn)_{m-1}}$$



$$\text{or } \cdot\underset{Ph}{\overset{Ph}{Sn}}-(\underset{Ph}{\overset{Ph}{Sn}})_{m-3}-\underset{Ph}{\overset{Ph}{Sn}}\cdot \qquad (1)$$

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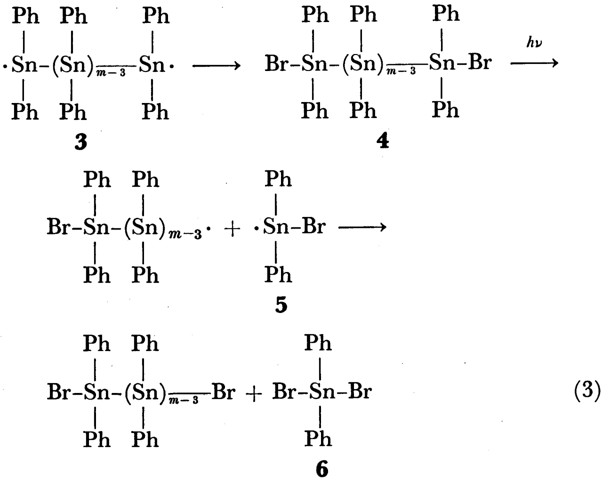
$$\underset{\mathbf{2}}{[Ph_2Sn:]} \xrightarrow{R'Br} Ph_2R'SnBr \qquad (2)$$

It is important to note that a considerable amount (20%) of diphenyltin dibromide was obtained. In contrast, photochemical reactions of dibutyltin with alkyl bromides gave only a low yield of dibutyltin dibromide (4%).[1] There seem to be two possible pathways for the formation of diphenyltin dibromide. (i) A part of diphenylstannylene might possess a biradical character (*i. e.*, in a triplet state) and abstract two bromine atoms from ethyl bromide to give the dibromide. Although the spin state of the stannylene cannot be discussed from our present results, the idea of triplet diphenylstannylene could offer one explanation for the formation of diphenyltin dibromide. (ii) Diphenylbromostannyl radical (**5**) formed by the photochemical cleavage of the Sn–Sn bond of the compound (**4**) could afford diphenyltin dibromide (Eq. 3). The possible intermediate, 1,2-dibromotetraphenylditin (**4**, $m=3$), could not be found in the reaction products. This compound could be completely consumed to give diphenyltin dibromide according to Eq. 3. This shows that the Sn–Sn bond of the tetraphenylditin compounds (**3**, **4**, $m=3$) could be cleaved by the UV irradiation in the case of diphenyltin derivatives. This is in sharp contrast to the case of dibutyltin, in which 1,2-dibromotetrabutylditin was formed in about 30% yield.[1]



$$\underset{\mathbf{3}}{\cdot\underset{Ph}{\overset{Ph}{Sn}}-(\underset{Ph}{\overset{Ph}{Sn}})_{m-3}-\underset{Ph}{\overset{Ph}{Sn}}\cdot} \longrightarrow \underset{\mathbf{4}}{Br-\underset{Ph}{\overset{Ph}{Sn}}-(\underset{Ph}{\overset{Ph}{Sn}})_{m-3}-\underset{Ph}{\overset{Ph}{Sn}}-Br} \xrightarrow{h\nu}$$

$$Br-\underset{Ph}{\overset{Ph}{Sn}}-(\underset{Ph}{\overset{Ph}{Sn}})_{m-3}\cdot + \underset{\mathbf{5}}{\cdot\underset{Ph}{\overset{Ph}{Sn}}-Br} \longrightarrow$$

$$Br-\underset{Ph}{\overset{Ph}{Sn}}-(\underset{Ph}{\overset{Ph}{Sn}})_{m-3}-Br + \underset{\mathbf{6}}{Br-\underset{Ph}{\overset{Ph}{Sn}}-Br} \qquad (3)$$

Another noticeable observation in the photolytic reaction of diphenyltin is the lower reactivity of diphenylstannylene compared with that of dibutylstannylene. The lower reactivity of diphenylstannylene might be implied by the following facts: A longer irradiation time was needed to achieve a high conversion, and diphenyltin did not react with alkyl monochlorides. Even after the irradiation of diphenyltin in propyl chloride for 90 min, the insertion product, $Ph_2PrSnCl$, was not detected in the reaction mixture. A low yield (26

TABLE 1. PHOTOCHEMICAL REACTIONS OF $(Ph_2Sn)_m$ WITH R′X

R′X	Yields of products (%)			
	$Ph_2R'SnX$	Ph_2SnX_2	$PhR'SnX_2$	Ph_3SnX
MeI	77	16	0	0
EtBr	64	20	2.6	2.2
PrBr	63	20	3.3	1.8
$BrCH_2Br$[a]	71	27	0	1.7
$ClCH_2Cl$	26	14	11	27

a) Distribution was determined by the integral values in the ^1H-NMR spectrum.

Table 2. Chemical shifts of $Ph_2R'SnX$ in ^{13}C-NMR spectra

$Ph_2R'SnX$	Chemical shifts (ppm) ($CDCl_3$)						
	Ph				R'		
	C_1	C_2	C_3	C_4	C_1	C_2	C_3
Ph_2MeSnI	a)	135.5	128.6	129.8	−3.1	—	—
$Ph_2EtSnBr$	a)	135.8	128.9	130.0	9.6	10.3	—
$Ph_2PrSnBr$	a)	135.9	129.1	130.6	20.0	19.6	18.2
$Ph_2(BrCH_2)SnBr$	a)	136.0	129.1	130.6	10.7	—	—
$Ph_2(ClCH_2)SnCl$	137.6	136.0	129.1	130.8	28.7	—	—

a) Undetected.

%) of the insertion product, $Ph_2(ClCH_2)SnCl$, was obtained in the reaction with dichloromethane.[5)]

All the results of the photochemical reactions of diphenyltin with alkyl halides and the ^{13}C-NMR spectral data of the insertion products are listed in Tables 1 and 2, respectively.

Photolysis of diphenyltin has been proved to be a more effective and facile method for the formation of diphenylstannylene than a thermal reaction of diphenyltin.[3)] In the thermal reaction, formation of diphenylstannylene was a minor reaction path and various disproportionation reactions predominated.

Experimental

The ^{13}C-NMR spectra were recorded in the pulse Fourier transform mode using a JEOL-FX 60 spectrometer operating at a resonance frequency of 15.03 MHz. The parameters used were: pulse width 8 μs, spectral width 2500 Hz for 8 K data points. Chemical shifts are given in ppm downfield from internal TMS.

The ^1H-NMR spectra were measured in deuteriochloroform with a Varian EM 360 spectrometer operating at 60 MHz.

Gas-liquid chromatography (GLC) was carried out at 230 °C using Apiezon grease L as a stationary phase.

Photolytic Reaction of Diphenyltin with Ethyl Bromide. Yellow crystalline diphenyltin[4)] (0.362 g) was dissolved in a large excess of ethyl bromide (8 ml) in a sealed pyrex glass ampoule, and was irradiated with a high pressure mercury lamp (450 W) at 0 °C under nitrogen atmosphere for 80 min. After irradiation, the excess of ethyl bromide was evaporated off to give a viscous liquid. The product was distilled *in vacuo* using a Kugelrohr (bath temperature was up to 200 °C) to give a trace of residue and a colorless distillate (0.813 g) containing $PhEtSnBr_2$, Ph_2SnBr_2, $Ph_2EtSnBr$, and Ph_3SnBr. These bromides were identified by the IR, ^1H-NMR,[3)] and ^{13}C-NMR spectra. A part of the distillate was treated with a large excess of methylmagnesium iodide in ether to convert the phenyltin bromides quantitatively into the phenylmethyltin derivatives. Distribution of the products was determined by GLC: $PhEtSnMe_2 : Ph_2SnMe_2 : Ph_2EtSnMe : Ph_3SnMe = 2.8 : 24.1 : 69.5 : 2.7$. It was confirmed that vacuum distillation caused no noticeable change in the distribution of the products.

The reactions with methyl iodide, propyl bromide, dichloromethane, and dibromomethane were carried out under similar conditions. In the reaction with methyl iodide, the product was treated with ethylmagnesium bromide for the determination of the distribution. In the reaction with dibromomethane, the product was distilled under high vacuum (0.02 Torr) to avoid the thermal decomposition. The distribution was determined by the integral values in the ^1H-NMR spectrum, since the methylation of $Ph_2(BrCH_2)SnBr$ with methylmagnesium iodide gave undetectable compounds on GLC analysis.

References

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5) Dichloromethane was found to be a more efficient trapping reagent of dibutylstannylene.[1)]