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Formation of Diorganostannylenes. I. Photolytic Reaction of Dibutyltin with Organic Halides

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The photochemical reactions of dibutyltin, $(Bu_2Sn)_m$, with alkyl monohalides, R′X, give $Bu_2R'SnX$-type compounds by the insertion of the intermediately formed dibutylstannylene to the C-X bond of alkyl halides. This provides a facile method for preparing $Bu_2R'SnX$ compounds, since the reaction proceeds quickly under mild conditions giving the products in good yields, the only by-product Bu_3SnX which can be distilled being obtained only in a low yield. The reactions with dihalomethanes were also successful. The reaction pathway is discussed in connection with the reactivities of the substrates.

In previous papers,[1,2] thermal reactions of polymeric diorganotins, $(R_2Sn)_m$, with alkyl halides, R′X, were reported to yield the insertion products, $R_2R'SnX$, together with a variety of disproportionation products, R_4Sn, R_3SnX, and $RR_2'SnX$. Kumada and his collabolators reported on the formation of silylenes, $R_2Si:$, by the photolysis of organopolysilanes.[3] Schroer and Neumann,[4] and Neumann and Schwarz[5] reported on the transient formation of dialkylstannylenes, $R_2Sn:$, by the thermal decomposition of 1,2-dichlorotetraalkylditin, and by the photolysis of dialkyltins, respectively. These reports have promped us to disclose our recent results of the photochemical reactions of dibutyltin with organic halides. This paper deals mainly with the reactions of dibutyltin with organic bromides and chlorides, giving a discussion on the reaction pathway comparing the results of the photolytic reactions with those of the thermal reactions.

A solution of dibutyltin, $(Bu_2Sn)_m$, in a large excess of alkyl bromides, R′Br, was irradiated with a high pressure mercury lamp through a Pyrex filter at 0 °C for 30 min to give $Bu_2R'SnBr$ in about 60% yield, together with a small amount of Bu_3SnBr (1—3%). From the distillation residue, bis(dibutylbromotin) oxide, $(Bu_2BrSn)_2O$, was isolated in about 30% yield. Yellow coloration of dibutyltin still remained when the solution was kept in the dark at room temperature for 10 days. Irradiation, therefore, apparently induced the reaction. The major product, $Bu_2R'SnBr$, could be formed by the insertion of transiently formed dibutylstannylene, $Bu_2Sn:$, into the C–Br bond of alkyl bromide. Since polymeric diorganotins are yellowish liquid or solids,[6] they have absorptions in the ultraviolet and visible regions (Fig. 1). The absorptions could be attributed to the polymeric Sn–Sn bonds. Thus, irradiation with UV light could cleave the Sn–Sn bonds of diorganotins. Photolysis of cyclic dibutyltin, $(Bu_2Sn)_m$, could produce dibutylstannylene, $Bu_2Sn:$, accompanied by the formation of cyclic dibutyltin, $(Bu_2Sn)_{m-1}$, and/or acyclic polydibutyltin biracdical (III) (Eq. 1). The spin state

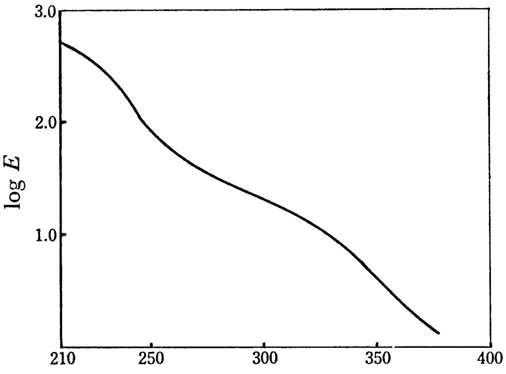
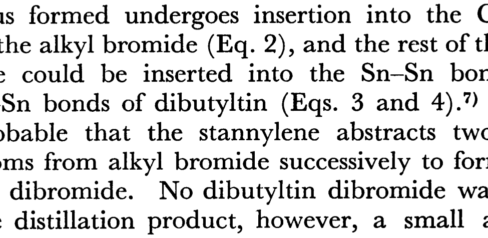
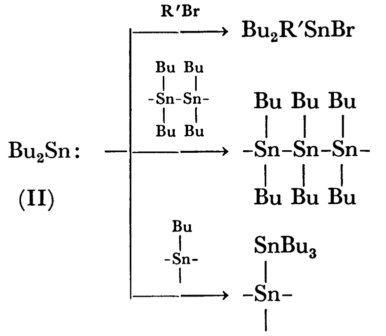


Fig. 1. Ultraviolet spectrum of dibutyltin in cyclohexane.



$$\underset{\text{(I)}}{(Bu_2Sn)_m} \xrightarrow{h\nu} \underset{\text{(II)}}{Bu_2Sn:} + \underset{\text{(I)}}{(Bu_2Sn)_{m-1}} \quad \text{or} \quad \underset{\text{(III)}}{\cdot\overset{Bu}{\underset{Bu}{Sn}}\text{—}(\overset{Bu}{\underset{Bu}{Sn}})_{m-3}\text{—}\overset{Bu}{\underset{Bu}{Sn}}\cdot} \tag{1}$$

of the stannylene, singlet or triplet can not be discussed from our present results. A part of the stannylene thus formed undergoes insertion into the C–Br bond of the alkyl bromide (Eq. 2), and the rest of the stannylene could be inserted into the Sn–Sn bonds and/or C–Sn bonds of dibutyltin (Eqs. 3 and 4).[7] It is also probable that the stannylene abstracts two bromine atoms from alkyl bromide successively to form dibutyltin dibromide. No dibutyltin dibromide was found in the distillation product, however, a small amount of the dibromide (*ca.* 4%) was detected in the reaction mixture (Eq. 5). A part of the dibromide could be consumed by the reaction with the stannylene (Eq. 6).



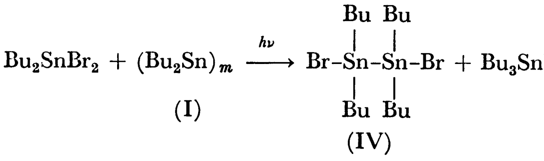
(2)

(3)

(4)

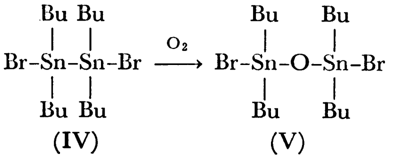
$$\underset{\text{(II)}}{Bu_2Sn:} \xrightarrow{2R'Br} Bu_2SnBr_2 + 2R'\cdot \tag{5}$$

It has been confirmed that dibutyltin dibromide readily reacts with dibutyltin under the same irradiation conditions to yield 1,2-dibromotetrabutylditin (IV) in 80% yield together with tributyltin bromide in 20% yield (Eq. 6). After the photolysis, the reaction mixture was exposed to air to oxidize the residual Sn–Sn bonds.[8] Thus, bis(dibutylbromotin) oxide (V) in the distillation residue should be formed by the air oxidation of 1,2-dibromotetrabutylditin (IV) (Eq. 7). Ditin compounds (IV) could be formed by the successive abstraction of two bromine atoms from alkyl bromide by tetrabutylditin biradical (Eq. 8), or by the reaction of dibutyltin dibromide with the stannylene (Eq. 6).



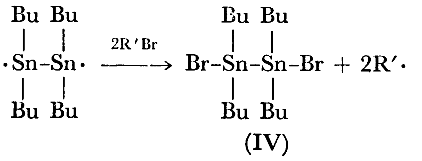
$$\mathrm{Bu_2SnBr_2} + (\mathrm{Bu_2Sn})_m \xrightarrow{h\nu} \mathrm{Br}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\mathrm{Br} + \mathrm{Bu_3SnBr} \qquad (6)$$

(I) (IV)



$$\mathrm{Br}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\mathrm{Br} \xrightarrow{\mathrm{O_2}} \mathrm{Br}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-O-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\mathrm{Br} \qquad (7)$$

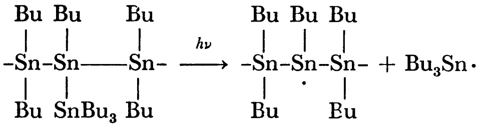
(IV) (V)



$$\cdot\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\cdot \xrightarrow{\mathrm{2R'Br}} \mathrm{Br}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\mathrm{Br} + 2\mathrm{R'}\cdot \qquad (8)$$

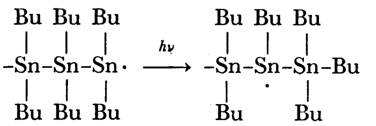
(IV)

The minor by-product, Bu_3SnBr, can be produced by the reaction of tributyltin radical with alkyl bromide. This reaction was found to occur in the dehalogenation of organic halides by organotin hydrides.[9] There might be several possible pathways for the formation of tributyltin radical. One of them is the insertion of dibutylstannylene into the Bu–Sn bond of dibutyltin to give tributyltin group (Eq. 4), which could be cleaved by the irradiation (Eq. 9). This insertion pathway, however, could be a minor one since the yield of Bu_3SnBr was independent of the concentration of $(Bu_2Sn)_m$.

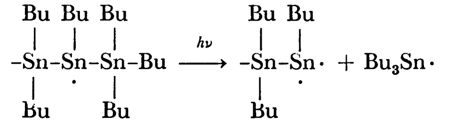


$$\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{SnBu_3}}{\mathrm{Sn}}}\text{——}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-} \xrightarrow{h\nu} \text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\cdot}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-} + \mathrm{Bu_3Sn}\cdot \qquad (9)$$

Another one is the intramolecular transposition of butyl group to give the tributyltin group at the terminal position together with the monobutyltin group (Eq. 10). The possibility of this pathway has been confirmed by the irradiation of polymeric dibutyltin in the absence of alkyl halide. By the photolysis of dibutyltin in benzene (0.503 g/8 ml) for 80 min, 9% of dibutyltin fragments were converted into tributyltin and monobutyltin fragments. In the case of the more dilute benzene solution (0.158 g/24 ml), the conversion proceeded more efficiently (23%). The disproportionation, therefore, would take place *via* the intramolecular process. This intramolecular transposition of butyl group might be a major pathway for the formation of tributyltin group. The tributyltin group thus formed is photochemically cleaved to afford tributyltin radical (Eq. 11).



$$\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\cdot \xrightarrow{h\nu} \text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\cdot}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-Bu} \qquad (10)$$

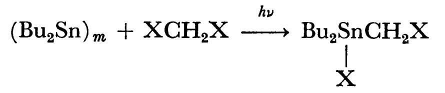


$$\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\cdot}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-Bu} \xrightarrow{h\nu} \text{-}\overset{\mathrm{Bu}}{\underset{\mathrm{Bu}}{\mathrm{Sn}}}\text{-}\overset{\mathrm{Bu}}{\underset{\cdot}{\mathrm{Sn}}}\cdot + \mathrm{Bu_3Sn}\cdot \qquad (11)$$

The reaction of dibutylstannylene with the free butyl radical cleaved photochemically from dibutyltin might be also possible. A similar photochemical disproportionation was reported in the photolysis of bis[bis(trimethylsilyl)methyl]stannylene to give the trisubstituted stannyl radical.[10] The probability of this pathway can not be eliminated by our present results.

In the reaction with propyl chloride, a longer reaction time was required to achieve a good conversion than in the cases of alkyl bromides. The insertion product, $Bu_2PrSnCl$, and the disproportionation product, Bu_3SnCl, were obtained in 57 and 7.3% yield, respectively. It is to be noted that the photochemical reaction occurred at lower temperature (0 °C), in shorter reaction time (80 min), in contrast to the thermal reaction,[1] where the insertion product, $Bu_2PrSnCl$, was produced under drastic conditions in the presence of catalysts (160 °C, 15 h) accompanied by many thermally scrambled alkyltin products. No bis(dibutylchlorotin) oxide was detected in the distillation residue exposed to air, but organopolystannoxane containing more than two tin atoms, presumably a trimer or a tetramer, was found. Since the C–Cl bond of alkyl chloride is less reactive than the C–Br bond, the rate of the insertion of dibutylstannylene toward the C–Cl bond could be much lower. In the reaction with alkyl chloride, accordingly, the reformation of Sn–Sn bonds from the stannylene (Eq. 3) could be enhanced. Therefore, the chance for the formation of tributyltin fragments increases, and the relatively longer chains of Sn–Sn bonds remain in the reaction mixture.

Dibutylstannylene also undergoes the insertion reaction into C–X bonds of dichloro- and dibromomethane to afford analytically pure dibutyl(chloromethyl)tin chloride (58%)[11] and dibutyl(bromomethyl)tin bromide (70%), respectively. No disproportionation products, Bu_3SnCl and Bu_3SnBr were detected in the reaction products. Since the stannylene was captured effectively by the dihalomethanes, the reformation reaction of polydibutyltin from the stannylene (Eq. 3) could be restricted, and the disproportionation to produce tributyltin fragment, therefore, might be extremely suppressed.



$$(\mathrm{Bu_2Sn})_m + \mathrm{XCH_2X} \xrightarrow{h\nu} \mathrm{Bu_2}\underset{\mathrm{X}}{\mathrm{Sn}}\mathrm{CH_2X} \qquad (12)$$

Experimental

Reactions with Alkyl Monohalides. Dibutyltin was prepared from dibutyltin dihydride and dibutyltin dimethoxide by the method of Neumann, Pedain, and Sommer.[12] In all the experiments, freshly prepared yellow liquid of dibutyltin was used. The ^{13}C-NMR spectra were recorded in the pulse Fourier transform mode with 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.

In a typical procedure, a mixture of 1.106 g of dibutyltin and 8 ml of ethyl bromide in a sealed Pyrex glass ampoule was irradiated with a high pressure mercury lamp (450 W) externally at 0 °C under nitrogen atmosphere for 30 min. The reaction mixture was then exposed to air, and the excess of ethyl bromide was removed by distillation *in vacuo*. The product was distilled under reduced pressure to give 0.946 g of distillate (bp 96—98 °C/3 mmHg), containing 57% yield of dibutylethyltin bromide and 1.1% of tributyltin bromide. Dibutylethyltin bromide was identified by comparing the retention time on gas chromatography and the IR and ^{13}C-NMR spectra with those of the authentic samples.[1] ^{13}C-NMR(CDCl$_3$): δ 9.6(Sn-**CH$_2$**CH$_3$ $J_{\text{C-}^{119}\text{Sn}}=334$ Hz), 10.3 (Sn-CH$_2$**CH$_3$**). The colorless crystals in the distillation residue (0.527 g, 35%) were recrystallized from acetone and identified as bis(dibutylbromotin) oxide, $(\text{Bu}_2\text{BrSn})_2\text{O}$.[13]

In a similar procedure, the reaction of dibutyltin with propyl bromide gave dibutylpropyltin bromide (66%),[1] tributyltin bromide (2.5%) and bis(dibutylbromotin) oxide (26%). Dibutylpropyltin bromide: ^{13}C-NMR(CDCl$_3$): δ 20.5 (Sn-**CH$_2$**CH$_2$CH$_3$ $J_{\text{C-}^{119}\text{Sn}}=338$ Hz), 19.4 (Sn-CH$_2$-**CH$_2$**CH$_3$), 18.3 (Sn-CH$_2$CH$_2$**CH$_3$**).

In the reaction with alkyl chlorides, the irradiation time was extended to 80 min. Thin-layer chromatography of the residual stannoxane developed with CH$_2$Cl$_2$ showed no detectable spot of bis(dibutylchlorotin) oxide, but those of longer chain stannoxanes in the lower R_f-values.

The reaction of 1.194 g of dibutyltin with 8 ml of propyl chloride gave dibutylpropyltin chloride (0.913 g, 57%),[1] tributyltin chloride (0.121 g, 7.3%) and residual stannoxane (0.412 g). Dibutylpropyltin chloride: ^{13}C-NMR(CDCl$_3$): δ 20.3 (Sn-**CH$_2$**CH$_2$CH$_3$ $J_{\text{C-}^{119}\text{Sn}}=338$ Hz), 19.4 (Sn-CH$_2$**CH$_2$**CH$_3$), 18.3 (Sn-CH$_2$CH$_2$**CH$_3$**).

Tributyltin chloride (1.063 g, 69%) was obtained in pure form, together with the residual stannoxane (0.326 g), from 1.107 g of dibutyltin and 8 ml of butyl chloride.

Reactions with Dihalomethanes. Under similar conditions, a solution of 3.24 g of dibutyltin in 10 ml of dichloromethane was irradiated for 30 min. Excess dichloromethane was evaporated off. Distillation of the residue gave analytically pure dibutyl(chloromethyl)tin chloride (bp 80—82 °C/0.01 Torr) in 58% yield (n_D^{25} : 1.5087, lit[11]). The compound was identified by elemental analysis, IR, PMR and ^{13}C-NMR spectra. PMR(CDCl$_3$) : δ 3.40 (s, 2H, CH$_2$Cl). ^{13}C-NMR(CDCl$_3$) : δ 29.3 (CH$_2$Cl, $J_{\text{C-}^{119}\text{Sn}}=$ 325 Hz). The reaction of dibutyltin and dibromomethane was carried out in a similar manner to give 70% yield of the new compound, dibutyl(bromomethyl)tin bromide, Bu$_2$-BrSnCH$_2$Br, (bp 87—88 °C/0.009 Torr, n_D^{25} : 1.5395). PMR (CDCl$_3$) : δ 3.00 (s, 2H, CH$_2$Br). ^{13}C-NMR(CDCl$_3$) : δ 11.8 (CH$_2$Br, $J_{\text{C-}^{119}\text{Sn}}=293$ Hz). Found: C, 26.30; H, 4.89%. Calcd for $\text{C}_9\text{H}_{20}\text{Br}_2\text{Sn}$: C, 26.56; H, 4.92%.

Reaction with Dibutyltin Dibromide. Dibutyltin dibromide (0.689 g) was added to the cyclohexane solution of dibutyltin (0.408 g) in a sealed Pyrex glass ampoule, and the mixture was irradiated under the same conditions. After the photolysis, the reaction mixture was exposed to air. A trace of organopolystannoxanes insoluble in CDCl$_3$ was removed by filtration. The gas chromatographic analysis and ^{13}C-NMR spectra showed that the reaction mixture consisted of bis(dibutylbromotin) oxide (80%) and tributyltin bromide (20%). The ratio of these compounds was determined by the integral values of their peaks assigned to the α-carbons of butyl groups in the ^{13}C-NMR spectra measured by gated decoupling technique without NOE. ^{13}C-NMR (CDCl$_3$) : δ 36.1, 36.3 (C(1) of $(\text{Bu}_2\text{BrSn})_2\text{O}$), 17.3 (C(1) of Bu$_3$SnBr).

Photolysis of Dibutyltin in the Absence of Alkyl Halide. The benzene solution of dibutyltin (0.503 g/8 ml) was irradiated for 80 min under the same conditions as above. To the irradiation product was added a benzene solution of iodine at 0 °C to cleave the Sn–Sn bond completely. The mixture was stirred for 5 min at 0 °C, and was treated with a large excess of methylmagnesium iodide. The distribution of the three products, BuMe$_3$Sn, Bu$_2$Me$_2$Sn, Bu$_3$MeSn, was determined by gas chromatographic analysis to be 4.6, 91, and 4.2%, respectively. When the diluted solution (0.158 g/24 ml) was irradiated, the distribution of the methylated products were found to be 11, 77, and 12%, respectively.

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