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DIORGANOSTANNYLENES

III *. FORMATION OF DIMETHYLSTANNYLENE FROM 1,1-DIMETHYL-2,3,4,5-TETRAPHENYL-1-STANNACYCLOPENTADIENE AND ACETYLENES

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Summary

Dimethylstannylene, $(CH_3)_2Sn$:, was formed transiently in the reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-stannacyclopentadiene (stannole) with dimethyl acetylenedicarboxylate or phenylacetylene. When this reaction was carried out in the presence of n-butyl bromide, dimethylstannylene inserted into the C—Br bond of n-butyl bromide to give n-butyldimethyltin bromide in 12% yield, but most of the dimethylstannylene was captured by dimethyl acetylenedicarboxylate to give a complex. The complex was also produced in the photolytic reaction of the dimethyltin polymer, $[(CH_3)_2Sn]_m$, with dimethyl acetylenedicarboxylate. With phenylacetylene, dimethylstannylene did not give a similar complex, but polymerized to give the dimethyltin polymer.

Introduction

Considerable work on the formation and reactions of organosilylenes has been published [2—9]. The pyrolysis of 7-silanorbornadienes is one method of generating dialkylsilylenes [2,3]. However, neither 7-germanorbornadiene nor R_2Ge-derived products was detected in reactions of a germacyclopentadiene with acetylenes [10].

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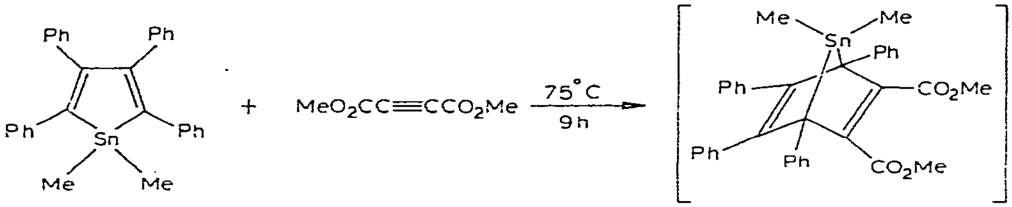
* For part II see ref. 1.

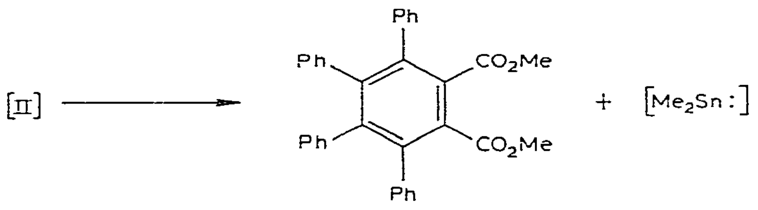
In the present work we present evidence for the formation of dimethylstannylene in the reaction of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-stannacyclopentadiene (I) (a stannole) with acetylenes. Dialkylstannylenes, $R_2Sn:$, generated by the pyrolysis of tetraalkyldihalodistannanes [11], or by photolysis of cyclic polydiorganotins [1,12,13], were captured by the alkyl halide, R'X, to give the triorganotin halide, $R_2R'SnX$.

Results and discussion

1,1-Dimethyl-2,3,4,5-tetraphenyl-1-stannacyclopentadiene (I) was brought into contact with dimethyl acetylenedicarboxylate at 75°C in the presence of a large excess of n-butyl bromide. In this reaction a 7-stannanorbornadiene adduct (II) could not be isolated. The products obtained were dimethyl tetraphenylphthalate (III) (96%), n-butyldimethyltin bromide (IV), a complex (possibly of the charge transfer type) of dimethylstannylene with the acetylene (V), and dimethyltin oxide. The phthalate III can be regarded as a decomposition product of the 1/1 adduct II. Only a small portion of dimethylstannylene was trapped by n-butyl bromide to give n-butyldimethyltin bromide (IV) in 12% yield. The major portion of the stannylene was captured by the acetylene to give a brown solid (V, 86%). The rest (1%) was converted into dimethyltin polymer, which was readily oxidized by atmospheric oxygen to give dimethyltin oxide when the reaction mixture was exposed to air. In this reaction, the formation of n-butyldimethyltin bromide (IV) leaves no room for doubt that the stannylene was formed transiently and subsequently inserted into the C—Br bond of n-butyl bromide.



(I) (II)



(III)

$$[\mathrm{Me_2Sn:}] + \mathrm{BuBr} \longrightarrow \mathrm{BuMe_2SnBr}$$

(IV)

$$[\mathrm{Me_2Sn:}] + \mathrm{MeO_2CC{\equiv}CCO_2Me} \longrightarrow [(\mathrm{Me_2Sn:})^{\delta+}(\mathrm{MeO_2CC{\equiv}CCO_2Me})^{\delta-}]_n$$

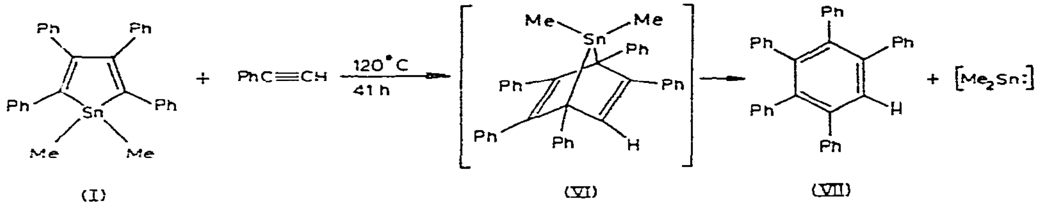
(V) brown precipitate

In the absence of n-butyl bromide, the reaction of I with dimethyl acetylenedicarboxylate (molar ratio 1/2) in benzene afforded III (95%), a brown solid (V, 89%) and dimethyltin oxide (8%). The complex V was an amorphous solid which was fairly soluble in methanol, acetone and tetrahydrofuran. The ultraviolet spectrum of the methanolic solution displayed broad absorptions up to the visible region having a shoulder at about 290 nm (ϵ 1040) and 380 nm (ϵ 530). The ^{1}H NMR spectrum of an acetone-d_6 solution of V showed a broad singlet at δ 0.62 and multiple peaks at 3.75 ppm assigned to the methyl protons of dimethyltin and methyl ester groups, respectively. The infrared spectrum of the complex showed characteristic bands of dimethyltin and carboxylate groups, but no band due to dimethyltin oxide at 580 cm^{-1}. The elemental analyses were consistent with 1/1 stoichiometric association of dimethylstannylene and the acetylenedicarboxylate. The molecular weight of V was determined in methanol solution to be 389 (0.010 M/kg) and 484 (0.020 M/kg). These values are much larger than that calculated for a monomeric 1/1 adduct (290.87), and are dependent on the concentration of the solution. This shows that complex is associated even in a polar solvent. On heating V up to 300°C, neither melting nor decomposition occurred. When a thin-layer chromatogram (silica gel) of complex V was developed in methanol or tetrahydrofuran, pronounced tailing of one point (R_f of the top of the point was 0.95) was observed. This might be due to the various degrees of the association of V. The Mössbauer spectrum for complex V consists of qaudrupole split doublet resonance (isomer shift 1.30 mm s^{-1}; quadrupole splitting 2.92 mm s^{-1}). Complex V exhibits much smaller isomer shift and larger quadrupole splitting than divalent tin compounds (*IS* 3.74, *QS* 0.86 mm s^{-1} for $(C_5H_5)_2Sn$: [14]). Compared with the Mössbauer spectra of complexes of diorganostannylenes with transition metal carbonyls [15], dicyclopentadienyltin with Lewis acids [10] and with π-acids [17], complex V does not belong to any types of the conventional complexes reported. The comparatively large quadrupole splitting may reflect the associated structure of V, suggested by the measured molecular weights. Addition of bromine to complex V in methanol yielded dimethyltin dibromide (98%), dimethyl acetylenedicarboxylate (10%), and the dibromide of the acetylenedicarboxylate (19%). This behavior also strongly indicates that complex V consists of dimethylstannylene and dimethyl acetylenedicarboxylate.

In this reaction, dimethylstannylene was captured almost quantitatively by the acetylene to form the stable complex V which resisted oxidation by atmospheric oxygen. When photolytic reaction of dimethyltin polymer with dimethyl acetylenedicarboxylate was carried out, the same complex as V was found to be produced whose physical data were identical to those of complex V prepared from the stannole.

The high electron-donating ability of the stannylene already has been shown in a number of diorganostannylene—transition metal complexes [15], dicyclopentadienyltin—Lewis acid complexes [16] and charge transfer complexes of bis(methylcyclopentadienyl)tin with strong π-acids [17]. Formation of a complex between dimethylstannylene and an electron-deficient acetylene has never before been reported.

The reaction of I with phenylacetylene in the presence of n-butyl bromide proceeded similarly. The adduct (VI), a supposed intermediate, however, could not be isolated. The products, obtained after exposure of the reaction mixture to air, were pentaphenylbenzene (VII, 95%), IV (18%) and dimethyltin oxide (77%). Transient formation of dimethylstannylene in this case also was confirmed by the formation of IV. No 1,4-distannacyclohexa-2,5-diene compounds were found among the reaction products. In contrast, silylenes are efficiently trapped by alkynes to give 1,4-disilacyclohexa-2,5-dienes and/or silacyclopropenes [2,3,7—9].



$$[\mathrm{Me_2Sn:}] \xrightarrow{\mathrm{BuBr}} \underset{\mathrm{(IV)}}{\mathrm{BuMe_2SnBr}} + (\mathrm{Me_2Sn})_m$$

In the absence of n-butyl bromide, the reaction of I with phenylacetylene gave VII and dimethyltin. No complex was obtained in this reaction. This might be attributed to the lesser electron-accepting ability of phenylacetylene as compared with the acetylenedicarboxylate.

Experimental

Reactions were conducted in sealed Pyrex tubes under a nitrogen atmosphere. The ^{1}H NMR spectra were recorded on a Varian EM 360 spectrometer operating at 60 MHz. The ^{13}C NMR spectra were measured in the pulse Fourier transform mode using a JEOL-FX60 spectrometer operating at a resonance frequency of 15.03 MHz. Chemical shifts were referred to tetramethylsilane. Gas-liquid chromatography (GLC) was run on an Apiezon grease L column at 120°C. Molecular weights were measured in methanol solution at 40.0°C by the vapor pressure equilibrium technique using Hitachi M-115 apparatus. The tin-119m Mössbauer spectrum was obtained at 110 K using a TMC-Mössbauer Drive Unit and an NS-Multichannel analyser (256 multichannel) against $\mathrm{Ba^{119m}SnO_3}$ sources. The isomer shift is quoted with respect to $\mathrm{SnO_2}$.

The stannole (I) was prepared by the method of Leavitt et al. [18]. The authentic n-butyldimethyltin bromide was prepared by the successive treatments of n-butyldimethyltin iodide [19] with aqueous sodium hydroxide, and with hydrobromic acid. Dimethyltin polymer was prepared from dimethyltin dichloride and lithium aluminum hydride in the presence of triethylamine by the method of Brown and Morgan [20].

Reaction of the stannole (I) with dimethyl acetylenedicarboxylate in the presence of n-butyl bromide

A solution of 0.270 g (0.535 mmol) of the stannole (I) and 0.164 g (1.16 mmol) of dimethyl acetylenedicarboxylate in 3.5 ml of n-butyl bromide was heated at 75°C for 9 h in a sealed tube under nitrogen. Subsequently, the reaction mixture was exposed to air overnight. Excess n-butyl bromide and n-butyldimethyltin bromide (IV) were distilled at reduced pressure and collected in an ice trap. The distillate was analyzed by GLC. n-Butyldimethyltin bromide (IV, 0.018 g, 12%), was found to be present. The distillation residue was extracted with MeOH. Evaporation of MeOH gave 0.133 g (86%) of a brownish-red, amorphous solid (V). The residue which was insoluble in MeOH consisted of 0.254 g (96%) of dimethyl tetraphenylphthalate (III), m.p. 259—260°C (lit. [21] 259—261°C), and a trace amount of dimethyltin oxide (1%). Compound III was identified by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. Dimethyltin oxide which is insoluble in benzene was separated from the residue by dissolving III in benzene.

Complex V gave the following physical data: IR (nujol); 1710s, 1580s, 1260s, 1190m, 1170m, 1030m, 900m, 780s, 550m, 525m. ^{1}H NMR; δ 0.62 (s, 6H), 3.75 ppm (m, 6H). UV (MeOH); 250 (a 2240), 300 (ϵ 910), 400 (ϵ 380), 500 (a 80), 600 nm (ϵ 30), shoulder at 290 (ϵ 1040) and 380 nm (ϵ 530). Mössbauer spectrum: *IS* 1.30 mm s^{-1}, *QS* 2.92 mm s^{-1}. Complex V did not melt below 300°C. Molecular weight (vapor pressure equilibrium method) (MeOH): Found, 484 (0.020 *M*/kg), 389 (0.010 *M*/kg); calcd., 290.87. (Found: C, 32.54; H, 3.83; Sn, 40.4, 40.6. $C_8H_{12}O_4Sn$ (1/1 complex) calcd.: C, 33.03; H, 4.16; Sn, 40.81%.)

A solution of 0.070 g (0.44 mmol) of bromine in tetrachloromethane (0.5 ml) was added to 0.055 g (0.19 mmol) of complex V in MeOH at 0°C. The color of bromine disappeared instantaneously. After 2 h, the reaction mixture was subjected to GLC analysis; dimethyltin dibromide (0.186 mmol, 98%), dimethyl acetylenedicarboxylate (0.019 mmol, 10%) and the dibromide of the acetylenedicarboxylate [22] (0.036 mmol, 19%) were detected. Distillation of the mixture (Kugelrohr) at 150°C/5 mmHg gave the above products and 0.017 g of an unidentified residue.

Reaction of the stannole (I) with dimethyl acetylenedicarboxylate (molar ratio 1/2) in the absence of n-butyl bromide

A mixture of 0.133 g (0.26 mmol) of I and 0.076 g (0.53 mmol) of dimethyl acetylenedicarboxylate was dissolved in benzene and heated at 75°C for 18 h. The reaction mixture was exposed to air overnight as above. The brown, benzene-insoluble solid which had formed was extracted with MeOH to give 0.035 g of V. The residue insoluble in MeOH was dimethyltin oxide (8%). The benzene solution was evaporated to leave a brown solid. Extraction of the latter with MeOH gave an additional portion (0.032 g) of V, and 0.123 g (95%) of a crystalline residue identified as III. The total yield of V was 89%.

Photolytic reaction of dimethyltin polymer with dimethyl acetylenedicarboxylate

A solution of 0.543 g of dimethyltin polymer and 0.583 g of dimethyl acetylenedicarboxylate in 20 ml of dry benzene was irradiated with a high pressure mercury lamp (450 W) externally at 15°C for 3 h in a sealed Pyrex tube under a nitrogen atmosphere. The brown reaction mixture was exposed to air. The benzene solution was concentrated to 7 ml and a brown material was precipitated by gradual addition of cyclohexane (40 ml). The precipitate was separated from the solvents by centrifugation. Benzene (15 ml) was added to dissolve the precipitate. About half of the precipitate remained undissolved, and the insoluble precipitate was removed off. The benzene solution was concentrated to

5 ml, and to the solution was added cyclohexane (20 ml) to reprecipitate the complex. Repetition of this procedure gave 0.147 g (14%) of a brown precipitate whose IR, ^{1}H NMR, UV spectra and elemental analyses were identical to those of complex V. When complex V was completely freed from solvents in vacuo, it became almost insoluble in benzene.

Reaction of I with phenylacetylene in the presence of n-butyl bromide

A solution of 0.262 g (0.52 mmol) of I and 0.609 g (6.0 mmol) of phenylacetylene in n-butyl bromide (4.0 ml) was heated at 120°C for 41 h. After exposing overnight the products to air, excess n-butyl bromide, phenylacetylene and the n-butyldimethyltin bromide which was formed were collected by vacuum distillation and subjected to GLC analysis. n-Butyldimethyltin bromide, 0.026 g (18%), was detected. The residue was extracted with benzene. The benzene extract gave 0.225 g (95%) of colorless crystals identified as pentaphenylbenzene (VII), m.p. 250—251°C (lit. [23] 251°C). The colorless residue insoluble in benzene was 0.065 g (76%) of dimethyltin oxide.

Reaction of I with phenylacetylene in the absence of n-butyl bromide

A solution of 0.057 g (0.11 mmol) of I and 0.365 g (3.58 mmol) of phenylacetylene was heated at 120°C for 65 h. Excess phenylacetylene was removed by distillation. The residual products were 0.048 g (95%) of VII and 0.017 g (92%) of dimethyltin oxide.

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