

ture for 14 hr. The product was filtered, washed with 95% ethanol, and recrystallized from a mixture of benzene and 95% ethanol to give 0.79 g. (70%) of yellow crystals, m.p. 180–183°.

*Anal.* Calcd. for  $C_{33}H_{26}N_2$ ; N, 6.22. Found: N, 6.19.

*1,5-Di(p-biphenyl)-3-(p-isopropylphenyl)-1,5-pentanedione.* A 75% solution of sodium ethoxide in 95% ethanol was added to a mixture of 3.0 g. of *p*-isopropylbenzaldehyde and 4.0 g. of *p*-phenylacetophenone in 75 ml. of 95% ethanol. After standing for 24 hr. the crude product was filtered, washed with water, and recrystallized from Cellosolve to give 4.2 g. (80.6%) of white needles, m.p. 210°.

*Anal.* Calcd. for  $C_{38}H_{34}O_2$ ; C, 87.32; H, 6.56. Found: C, 86.91; H, 6.56.

*1-Phenyl-3-(p-biphenyl)-5-(p-isopropylphenyl)-2-pyrazoline.* A solution of 5.0 g. of 1,5-di(*p*-biphenyl)-3-(*p*-isopropylphenyl)-1,5-pentanedione and 1.1 g. of phenylhydrazine in 25 ml. of glacial acetic acid was heated at 80° for 2 hr. After cooling to room temperature the product was filtered, washed with water, and recrystallized once from benzene and twice from 95% ethanol to give 1.2 g. (55%) of yellow plates, m.p. 167°.

*Anal.* Calcd. for  $C_{30}H_{28}N_2$ ; N, 6.73. Found: N, 6.58.

*Ultraviolet and infrared absorption data.* The ultraviolet absorption measurements were made with Beckman DU and DK-2 spectrophotometers using 1.00-cm. silica cells and hydrogen discharge light sources. Absolute methanol solutions were used. The infrared spectral measurements were made with a Baird double beam recording spectrometer using potassium bromide pellets.

*Acknowledgment.* This research was supported in part by the Atomic Energy Commission under Contract No. AT-(40-1)-2162 between the University of Louisville and the Atomic Energy Commission. The authors acknowledge this support and also express their appreciation to the National Science Foundation for Grant NSF-G4074 which provided a recording ultraviolet spectrophotometer.

LOUISVILLE, KY.  
LOS ALAMOS, N. M.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

## 1,1-Diethoxy-3-(triphenylstannyl)-2-propyne

O. H. JOHNSON<sup>1</sup> AND J. R. HOLUM<sup>2</sup>

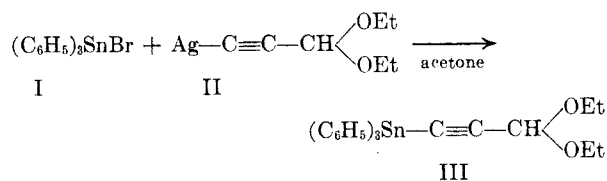
Received November 7, 1957

The synthesis and properties of an acetylenic tin compound containing a potential aldehyde group are presented.

The only organotin derivatives of acetylene, bis(triphenyltin)acetylene and bis(triethyltin)acetylene, found in the literature were reported by Beermann and Hartmann.<sup>3</sup> These two acetylenic tin compounds were found to have weak tin-carbon bonds. The ethyl derivative slowly hydrolyzed to triethyltin hydroxide and acetylene. Both reacted readily with base forming triorganotin hydroxides and acetylene. Acids also split the tin-carbon bond. In the presence of silver ion or ammoniacal copper(I) ion, silver or copper(I) acetylide formed. Iodine also broke the tin-carbon bond. Ethylmagnesium bromide reacted with bis(triphenyltin)acetylene to form ethyltriphenyltin and acetylenedimagnesium bromide. The stability of both the trialkyl or triaryl tin cation and the acetylenic anion contributed greatly to the ease of cleavage of the tin-carbon bonds in these cases.

We have prepared an acetylenic organotin compound containing a potential aldehyde group and have found that the tin-carbon bond wherein the

carbon atom is part of an acetylenic linkage is indeed very readily broken. 1,1-Diethoxy-3-(triphenylstannyl)-2-propyne, III, was prepared by the action of the silver salt of propionaldehyde diethylacetal, II, on triphenyltin bromide, I,



The structure of 1,1-diethoxy-3-(triphenylstannyl)-2-propyne was assigned primarily on the basis of origin and analytical data. Its infrared spectrum in chloroform did not show absorption in the region 2000–2400  $cm^{-1}$  but this does not rule out the possible existence of a disubstituted acetylene.<sup>4</sup> The chemical behavior indicated a very weak tin-carbon bond. Action of dilute hydrochloric acid (1%) gave triphenyltin chloride. Dilute alkali reacted with 1,1-diethoxy-3-(triphenylstannyl)-2-propyne to give triphenyltin hydroxide. The search for other products was not fruitful. Attempts to prepare a 2,4-dinitrophenylhydrazone of 1,1-diethoxy-3-(triphenylstannyl)-2-propyne by *in situ* hydrolysis of the acetal linkage was unsuccessful and a control experiment with

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)-984.

(2) Supported by a Grant-in-Aid of Research from the Graduate School of the University of Minnesota. Present address: Department of Chemistry, Augsburg College, Minneapolis 6, Minnesota.

(3) C. Beermann and H. Hartmann, *Z. anorg. Chem.*, **276**, 20 (1954).

(4) L. J. Bellamy, *The Infra-Red Spectra of Complex Molecules*, Methuen & Co. Ltd., London, 1954, pp. 48–53.

propionaldehyde diethyl acetal also did not respond under those conditions.

In the presence of palladium on carbon, 1,1-diethoxy-3-(triphenylstannyl)-2-propyne absorbed three moles of hydrogen per mole at room temperature and a pressure of slightly above atmospheric pressure. These results are consistent with the structure assigned if one mole of hydrogen cleaved the tin-carbon bond.

Attempts to prepare 1,1-diethoxy-3-(triphenylstannyl)-2-propyne by the action of the Grignard derivative of propionaldehyde diethylacetal on either triphenyltin chloride or triphenyltin bromide were not successful. When the bromomagnesium derivative of the acetylenic acetal was used with triphenyltin chloride, the principal product was triphenyltin bromide which formed in a yield of 59%. When tri-*n*-butyltin chloride was used instead of triphenyltin chloride, a similar reaction occurred and tri-*n*-butyltin bromide was isolated in 46% yield. Use of triphenyltin bromide and a catalytic amount of copper(I) bromide with the bromomagnesium Grignard reagent gave no isolable product.

During the course of these studies, it was found that the infrared spectra of chloroform solutions of triphenyltin chloride and triphenyltin bromide were identical within the range 650  $\text{cm}^{-1}$  to 3500  $\text{cm}^{-1}$ .

#### EXPERIMENTAL

*Propionaldehyde diethylacetal.* This compound was prepared from acrolein by a modification of the method of Grard.<sup>5</sup> The method involved bromination of acrolein, conversion of the resulting  $\alpha,\beta$ -dibromopropionaldehyde to its diethylacetal by action of ethyl orthoformate and dehydrobromination of the product in concentrated alcoholic potassium hydroxide.

Acrolein (112 g., 2 moles, Tech.) was stirred and cooled (ice bath) while bromine (320 g., 2 moles) was added dropwise over a period of 5.5 hr. Ethyl orthoformate (328 g., 2.2 moles, C & B reagent) and absolute ethanol (276 g., 6 moles), both chilled to ice bath temperature, were added. The solution was stirred and cooled for 1 hr. and then placed in the refrigerator for 4 days. The volume was reduced *in vacuo* until the temperature of the distillate reached 98° at 7 mm. to insure removal of unreacted ethyl orthoformate. The residue, crude  $\alpha,\beta$ -dibromopropionaldehyde diethyl acetal (max. of 2 moles) was cooled and added in a thin stream to a chilled, stirred solution of potassium hydroxide (280 g. of 85% min. KOH, minimum of 238 g. KOH, 4.25 moles) in absolute ethanol (1900 ml.). The mixture was stirred as it warmed to room temperature. After 1 hr., it was filtered. The solid was collected and washed with ethanol (100 ml.). The ethanol was added to the filtrate and the solution was allowed to remain at room temperature overnight. It was then stirred and refluxed 6 hr. During the last 1.5 hr. of this period, ethanol (1 l.) was collected by distillation. To facilitate isolation of the product, the mixture was divided into two equal aliquots and each was processed as follows: The aliquot was poured into cold water (3 l.) and extracted with chloroform (four 300-ml. portions). The chloroform extracts from both aliquots were

combined, washed with water (two 200-ml. portions), and dried ( $\text{CaCl}_2$ ). The chloroform was removed at atmospheric pressure and the residue fractionated through a 20 cm. spiral glass column. The product (116.5 g., 0.91 mole, 45% from acrolein) was collected as a colorless liquid at 70–72°/70 mm. A portion was redistilled, b.p. 82°/109 mm.,  $n_D^{25}$  1.4106.

*Silver salt of propionaldehyde diethylacetal.* Grard's procedure<sup>5</sup> was used with slight modification. A solution of ammoniacal silver nitrate (from 13.6 g., 0.08 mole,  $\text{AgNO}_3$ , together with just enough dilute ammonium hydroxide to effect solution) in water (approx. 100 ml. total volume) was stirred while a solution of freshly distilled propionaldehyde diethyl acetal (9.6 g., 0.075 mole) in an equal volume of acetone was added dropwise over a period of 45 min. (When acetone was omitted, the precipitate became gummy.) The white solid which separated was collected on a filter, washed twice with water, and recrystallized from abs. ethanol. When dry, it weighed 13.4 g. (76%) and had a grayish cast.

*Action of the silver salt of propionaldehyde diethylacetal on triphenyltin bromide.* 1,1-Diethoxy-3-(triphenylstannyl)-2-propyne. A solution of the silver salt of propionaldehyde diethylacetal (10 g., 0.43 mole) in warm acetone (75 ml.) was stirred while a solution of triphenyltin bromide (18 g., 0.43 mole) in acetone (75 ml.) was added dropwise. The mixture was stirred 90 min. and then allowed to stand overnight at room temperature. The clear supernatant liquid was decanted from the grayish precipitate and the acetone was removed under reduced pressure. A clear, almost colorless oil remained which gradually solidified. After drying *in vacuo*, the solid weighed 16.3 g. and after two crystallizations from petroleum ether-B (b.p. 60–68°) melted at 58–60° (uncorr.).

*Anal.* Calcd. for  $\text{C}_{25}\text{H}_{26}\text{O}_2\text{Sn}$ : C, 62.9; H, 5.49; Sn, 24.9; —OEt, 18.9; mol. wt. 477. Found: C, 62.8, 62.3; H, 4.91, 5.50; Sn, 25.4, 25.4; —OEt, 16.3; mol. wt., 458, 454.<sup>6</sup>

The product gave a negative Beilstein test, rapidly absorbed bromine in carbon tetrachloride and reduced potassium permanganate. It gave a positive Zeisel test.<sup>7</sup> The standard procedure for the preparation of a 2,4-dinitrophenylhydrazone of an aldehyde involving in this case *in situ* hydrolysis of the acetal linkage gave no precipitate.<sup>8</sup> Propionaldehyde diethylacetal under the same conditions also gave no precipitate.

In absolute ethanol (15 ml.) containing 10% palladium on charcoal (approx. 100 mg.), 1,1-diethoxy-3-(triphenylstannyl)-2-propyne (500 mg.,  $1.05 \times 10^{-3}$  moles) absorbed  $3.18 \times 10^{-3}$  moles of hydrogen at a temperature of 26–29° and a pressure of 734 mm. This represents an uptake of 3.03 moles hydrogen per mole if the molecular weight is taken as 477.

*Action of dilute hydrochloric acid on 1,1-diethoxy-3-(triphenylstannyl)-2-propyne.* Water (5 ml.) was added to a solution of 1,1-diethoxy-3-(triphenylstannyl)-2-propyne (4.4 g.,  $9.2 \times 10^{-3}$  mole) in acetone (20 ml.). To this solution 10% aqueous hydrochloric acid (3 ml.) was added. The mixture was cloudy but became clear when warmed. It was boiled for 5 min. and poured into ice water (700 ml.). Collection of the solid on a filter and drying *in vacuo* over phosphorous pentoxide resulted in 3.6 grams of a solid melting at 85–95° (uncorr.). Two recrystallizations from petroleum ether-B (b.p. 60–68°) raised the melting point to 105.5–107.5° (uncorr.). A mixed melting point with

(6) Microanalytical results for C, H and —OEt are from two different laboratories. One laboratory reported that the compound exploded during the analysis.

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th Ed., John Wiley and Sons, New York, 1956, p. 116.

(8) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th Ed., John Wiley and Sons, New York, 1956, p. 219.

(5) J. Grard, *Ann. chim.*, **13**, 337 (1930); see also J. C. Sheehan and C. A. Robinson, *J. Am. Chem. Soc.*, **71**, 1436 (1949).

authentic triphenyltin chloride, m.p. 106–107° (uncorr.), was not depressed.

*Action of potassium permanganate on 1,1-diethoxy-3-(triphenylstannyl)-2-propyne.* A solution of 1,1-diethoxy-3-(triphenylstannyl)-2-propyne (2.4 g.) in acetone (25 ml.) was stirred while 10% aqueous potassium permanganate (10 ml.) was added portionwise. The color was discharged and manganese dioxide formed. More potassium permanganate was added in the form of a saturated solution in acetone until the color persisted two minutes at room temperature. The solids were separated and the filtrate evaporated. Glistening white crystals of triphenyltin hydroxide, identified by m.p. and origin, remained and were washed and dried at 80°; weight, 1.4 g. (77%), m.p. 115–121° (uncorr.). After one crystallization from ethanol, the solid was snow white and melted at 120–120.5° (uncorr.). Triphenyltin hydroxide melts at 119–120° (uncorr.).<sup>9</sup>

*Action of the bromomagnesium derivative of propionaldehyde diethylacetal on triphenyltin chloride.* Grard's procedure for the preparation of the Grignard reagent was used.<sup>5</sup> A solution of ethylmagnesium bromide (from 8.4 g. magnesium, 0.34 g.-atom) in ether (100 ml.) was added dropwise to a stirred, cooled (ice bath) solution of propionaldehyde diethylacetal (44 g., 0.34 mole) in ether (950 ml.). Evolution of ethane occurred smoothly. When the addition of ethylmagnesium bromide was completed, the ice bath was removed and the mixture was refluxed 1 hr. A grayish viscous mass separated early in this operation. To the stirred, refluxing mixture triphenyltin chloride (115 g., 0.34 mole) was added as follows: Approximately one third was added in the form of a saturated solution in ether (total vol., 1 liter). A reaction occurred with the addition of each drop of triphenyltin chloride solution, as evidenced by the appearance of cloudiness. The remainder of the triphenyltin chloride was added as the solid in one portion. The mixture was stirred and refluxed 1.5 hr. and then it remained at room temperature overnight, after which it was stirred and refluxed during the next day and set aside at room temperature overnight.

The mixture was filtered and the filtrate concentrated to 500 ml. and filtered. The filtrate was cooled and a tan solid separated weighing 47 g. and melting at 118–122° (uncorr.) when dry. After one recrystallization from carbon tetrachloride, it melted at 121–122° (uncorr.). Evaporation of the filtrate gave 39 g. more of the solid melting at 118–121° (uncorr.); total yield, 86 g. (59%). It gave a positive sodium fusion test for bromine. A mixed melting point of this compound with an authentic sample of triphenyltin bromide was not depressed.

*Anal.* Calcd. for  $C_{18}H_{16}SnBr$ : C, 50.3; H, 3.5; Sn, 27.6; Br, 18.6; mol. wt., 430. Found: C, 50.6; H, 3.60; Sn, 28.1, 28.3, 27.8, 27.8; Br, 18.0, 18.2, 18.4, 18.6; mol. wt., 410, 409.

The infrared spectrum of this product in chloroform was indistinguishable from the spectra of either authentic triphenyltin bromide or triphenyltin chloride in chloroform.

In another experiment in which benzene replaced the ether as the "solvent" for the Grignard derivative of propionaldehyde diethylacetal, the same product, triphenyltin bromide, formed in a yield of 52%.

*Action of the bromomagnesium derivative of propionaldehyde diethylacetal on tri-*n*-butyltin chloride.* Ethylmagnesium bromide (from 2.7 g., 0.11 g. atom magnesium) in ether (approx. 50 ml.) was added dropwise over a period of 25 min. to a cooled, stirred solution of freshly distilled propionaldehyde diethylacetal (12.8 g., 0.10 mole) in thiophene-free benzene (150 ml.). The mixture was allowed to warm to room temperature and was stirred 1 hr. until the evolution of ethane ceased. The mixture of the viscous, gummy Grignard derivative and benzene was stirred while a solution of freshly distilled tri-*n*-butyltin chloride (32.4 g., 0.10 mole, b.p. 138–9°/4.5 mm.,  $n_D^{25}$  1.4883) in thiophene-free benzene (100 ml.) was added dropwise. The gummy Grignard reagent was slowly consumed, the mixture became opaque, and a brownish solid separated. The mixture was filtered and the filtrate was fractionated *in vacuo* using a 10-cm. Vigreux column. At 105–110°/0.55 mm. a colorless oil was collected which weighed 17 g.,  $n_D^{25}$  1.4984. This oil gave a positive Beilstein test and an instantaneous precipitate with sodium iodide in acetone. A sodium fusion test for bromine was positive. Authentic tri-*n*-butyltin bromide has a refractive index of  $n_D^{25}$  1.5000.<sup>10</sup> For tri-*n*-butyltin chloride,  $n_D^{25}$  1.4908 has been reported.<sup>11</sup> On the basis of these data, it was concluded that the oil was tri-*n*-butyltin bromide. Accordingly, the yield was 46% of the theoretical. The residue was very viscous and brownish-black. Further distillation was accompanied by considerable decomposition, but at 133–316°/4 mm., an unidentified yellow oil weighing 3.5 g.,  $n_D^{25}$  1.4799 was obtained.

*Acknowledgment.* The authors wish to thank Mr. Thomas Severeid for performing the tin analyses, determining the molecular weights and preparing tri-*n*-butyltin chloride and tri-*n*-butyltin bromide.

MINNEAPOLIS 14, MINN.

(9) E. Krause and A. V. Grosse, *Die Chemie der Metall-Organischen Verbindungen*, Gebrüder Borntraeger, Berlin, 1937, p. 343.

(10) W. J. Jones, D. P. Evans, T. Gulwell, and D. C. Griffiths, *J. Chem. Soc.*, 1935, 45.

(11) Z. M. Manulkin, *J. Gen. Chem. (U.S.S.R.)*, 18, 299 (1948); *Chem. Abstr.*, 42, 6742 (1948).