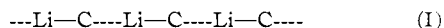


lie at frequencies outside the sodium chloride region, since all of the bands reported by Shigorin² have been shown not to be C-Li bands. Moreover, Shigorin's spectra of methyl lithium vapor show no sign of the rotational fine structure² which would be expected for molecules as simple as CH₃Li.

In their papers Rodionov and Shigorin describe the polymerization of organolithium compounds in terms of the formation of "lithium bonds" (I), analogous to hydrogen bonds, which bring about



cyclic or linear association of these compounds in solution.^{2,3} However, the strong association of alkyllithium compounds, persisting even in the

vapor phase, suggests (as Brown and Rogers earlier proposed¹) that association of organolithium compounds takes place through the formation of multi-center electron-deficient bonds of the same type which occur in Al₂(CH₃)₆ and Be(CH₃)_{2x}. In the light of the evidence now available, we see no reason for regarding the bonds in alkyllithium polymers as essentially different from other electron-deficient bonds or in designating them by a special name.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

The Preparation of Organolithium Compounds by the Transmetalation Reaction. I. Vinyllithium^{1,2}

BY DIETMAR SEYFERTH AND MICHAEL A. WEINER

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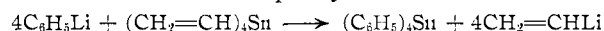
The transmetalation reaction occurring between phenyllithium and tetravinyltin (4:1 molar ratio) in ether produces vinyllithium in good yield. A similar reaction occurs between *n*-butyllithium and tetravinyltin in pentane; in this case solid vinyllithium precipitates. Vinyllithium is more stable in ether and tetrahydrofuran solution than are *n*-butyllithium or phenyllithium. The use of vinyllithium in the preparation of a number of previously known vinyl compounds, as well as of the new [B(CH=CH₂)₄]⁻ and [B(CH=CH₂)(C₆H₅)₃]⁻ ions, is described.

The exchange of organic groups between an organolithium compound and an organic derivative of a heavy metal (R₂Hg, R₃Tl, R₄Sn, R₄Pb, R₃Sb, R₃Bi) represents a route to organolithium reagents which up to the present time has had only very little synthetic application. Many examples of this reaction, which was reported first by Schlenk and Holtz,³ have been given. In nearly all examples cited, the lithium reagent produced in this exchange reaction was more conveniently prepared by the more common methods used in the synthesis of organolithium compounds.

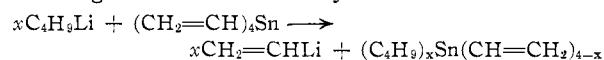
We have used the transmetalation reaction to prepare a number of novel organolithium reagents which are either difficult or impossible to prepare by other methods: vinyllithium,¹ allyllithium,⁴ perfluorovinyllithium⁵ and others. The present report is concerned with the preparation and some reactions of vinyllithium.⁶

We have found that the transmetalation reaction between a vinyltin compound and an alkyl- or aryllithium compound represents a very versatile procedure for preparing vinyllithium either in solution or in solid form. Most convenient for

most synthetic purposes is the preparation of vinyllithium in diethyl ether solution. The most practical starting material is tetravinyltin, which became available in developmental quantities⁷ during the late stages of this research. The reaction between phenyllithium and tetravinyltin (4:1 molar ratio) in ether solution proceeded essentially to completion within 30 minutes; tetraphenyltin precipitated in *ca.* 95% yield, and a solution of vinyllithium containing also lithium bromide (from the phenyllithium preparation) and minor amounts of tetraphenyltin⁸ remained



In some cases vinyllithium solutions free of these impurities were needed. This requirement was met when vinyllithium was prepared in pentane using *n*-butyllithium. Treatment of tetravinyltin with *n*-butyllithium in pentane also resulted in an exchange reaction. In the system



the organotin compounds and *n*-butyllithium are liquids soluble in pentane, while vinyllithium, a solid, is not very soluble in pentane and precipitates from solution. The solid vinyllithium can be filtered (under nitrogen: it is pyrophoric in air), washed free of soluble contaminants and dissolved in the desired solvent. This exchange reaction does not go to completion, and a butyllithium/

(7) The current suppliers are Metal and Thermit Corporation and Peninsular ChemResearch, Inc.

(8) Tetraphenyltin is soluble to the extent of 0.102 g. per 100 ml. of diethyl ether at 20°: W. Strohmeier and K. Miltenberger. *Chem. Ber.*, **91**, 1357 (1958).

(1) Preliminary communication: D. Seyferth and M. A. Weiner, *Chemistry and Industry (London)*, 402 (1959).

(2) Also Part X of the series, "Vinyl Derivatives of Metals"; Part IX, D. Seyferth, G. Raab and K. A. Brändle, *J. Org. Chem.*, **26**, in press (1961).

(3) W. Schlenk and J. Holtz, *Ber.*, **50**, 262 (1917).

(4) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959).

(5) D. Seyferth, T. Wada and G. Raab, *Tetrahedron Letters*, No. 22, 20 (1960).

(6) A review of previous attempts to prepare vinyllithium is given by D. Seyferth in "Vinyl Compounds of Metals," in "Progress in Inorganic Chemistry," Vol. III, F. A. Cotton, editor, Interscience Publishers, Inc., New York, N. Y., 1961.

tetravinyltin ratio of 2-2.5 was found to give best results.

Solid vinylolithium has been prepared in the pure, unsolvated state by evaporating ethereal vinylolithium solutions prepared by the tetravinyllead-lithium reaction.⁹ There was some doubt about the stability of solid vinylolithium. Thus it was reported⁹ that the pyrophoric nature of small samples of solid vinylolithium decreased as the compound was allowed to age under a nitrogen atmosphere. Also, changes in the C=C stretching frequency of vinylolithium were reported to occur as the solid was allowed to age. This behavior was ascribed tentatively to polymerization of vinylolithium in the solid state.⁹ In view of these results, the aging of solid vinylolithium was investigated further. A freshly prepared sample of solid vinylolithium (*ca.* 0.1 g.) was hydrolyzed, and the evolved gases were determined mass spectrometrically to consist of over 95% ethylene. After aging the solid vinylolithium for 36 hr. under nitrogen, the same results were observed on hydrolysis of the sample. After seven days a similar sample had become yellow, and only about one-fifth as much gas was liberated on hydrolysis; the gas was >95% ethylene. A fourth sample was aged under nitrogen for 18 days. After this time it had become orange, and only a very low yield of gas resulted on hydrolysis. The mass spectrum of the gaseous products showed the presence of C₄, C₆ and C₈ hydrocarbons in addition to ethylene. On the other hand, when a much larger sample (*ca.* 2.5 g.) of vinylolithium was allowed to age for 13 days and then dissolved in ether and treated with triphenylchlorosilane, a 68% yield of triphenylvinylsilane was obtained. This result would indicate that bulk samples of solid vinylolithium are fairly stable. All other results were obtained with small samples of vinylolithium in the form of thin layers of solid, and it is possible that the observations which suggested a gradual disappearance of vinylolithium in these samples may be the result not of a solid-state polymerization reaction but of slow oxidation of the vinylolithium by the very low oxygen content of the prepurified nitrogen used.

Of particular interest with regard to the synthetic utility of vinylolithium in solution was the question of its stability in ether solvents. The more reactive organolithium reagents such as *n*-butyllithium react with diethyl ether at room temperature at a rate sufficiently fast to require their utilization within a short time after their preparation,¹⁰ and even the less reactive aryllithium compounds cleave tetrahydrofuran at room temperature.¹¹ However, solutions of vinylolithium were found to be quite stable, with little decomposition of the reagent occurring in diethyl ether or in tetrahydrofuran at room temperature during one week. Thus vinylolithium appears to be relatively unreactive in lithium-hydrogen exchange reactions. However, vinylolithium in ether reacted normally with a variety of metallic and organometallic halides, as well as with ketones and with carbon dioxide.

(9) E. C. Juenge and D. Seyferth, *J. Org. Chem.*, **26**, 563 (1961).

(10) H. Gilman, A. H. Haubein and H. Hartzfeld, *ibid.*, **19**, 1034 (1954).

(11) H. Gilman and B. J. Caj, *ibid.*, **22**, 1165 (1957).

Some of the reactions of vinylolithium with various substrates are summarized in Table I.

TABLE I

REACTIONS OF VINYLITHIUM IN ETHER SOLUTION		
Substrate	Product	Yield, % ^a
(<i>n</i> -C ₄ H ₉) ₃ SnCl	(<i>n</i> -C ₄ H ₉) ₃ SnCH=CH ₂	74
(C ₆ H ₅) ₃ SiCl	(C ₆ H ₅) ₃ SiCH=CH ₂	68
(C ₂ H ₅) ₃ SiCl	(C ₂ H ₅) ₃ SiCH=CH ₂	57
(CH ₃) ₂ SiCl ₂	(CH ₃) ₂ Si(CH=CH ₂) ₂	39
(C ₆ H ₅) ₃ GeBr	(C ₆ H ₅) ₃ GeCH=CH ₂	76
AsCl ₃	(CH ₂ =CH) ₂ As	51
BI ₃	Li[B(CH=CH ₂) ₄] ^{b,c}	
B(C ₆ H ₅) ₃	Li[B(CH=CH ₂)(C ₆ H ₅) ₃] ^{b,d}	
(CH ₃) ₂ C=O	(CH ₃) ₂ (CH ₂ =CH)COH	74
CO ₂	CH ₂ =CHCO ₂ H	37

^a Based on the amount of substrate used. ^b Isolated as the [(C₆H₅)₃CH₃P] salt. ^c Isolated as the [(C₆H₅)₃CH₃As] salt. ^d Isolated as the [(CH₃)₄N] salt.

Since vinylolithium was found to be considerably more stable than phenyllithium in tetrahydrofuran, the possibility of carrying out the transmetalation reaction in this solvent was investigated briefly. It was found that the exchange reaction between phenyllithium and triphenylvinyltin does not proceed smoothly in tetrahydrofuran. This is at least partially due to an apparent reaction of tetraphenyltin with vinylolithium in this solvent. Upon adding a vinylolithium solution in tetrahydrofuran to a suspension of tetraphenyltin in this solvent, the tetraphenyltin went completely into solution, and only 49% of the original tetraphenyltin could be recovered.

In summary, the synthesis of vinylolithium by the transmetalation procedure is of special value, since it allows the preparation of a reactive vinylating agent in solvents in which the vinylmagnesium halides cannot be prepared. Furthermore, this method makes possible the preparation of pure, solid vinylolithium. In this way vinylolithium nicely complements the vinyl Grignard reagents. This procedure for preparing vinylolithium seems to us to be more satisfactory than the recently reported¹² preparations by the action of vinyl chloride on metallic lithium containing 2% sodium (a reaction requiring THF as the solvent and thus offering few advantages over the vinyl Grignard reagent) or by the reactions of metallic lithium with the very toxic divinylmercury¹³ and the difficult to prepare tetravinyllead.⁹

Experimental¹⁴

Preparation of Vinylolithium from Tetravinyltin and Phenyllithium in Diethyl Ether, and its Reaction with Tri-*n*-butyltin Chloride.—A solution of 87 ml. of 1.15 *M* phenyllithium in ether (0.1 mole) was added rapidly to 5.7 g. (0.025 mole) of tetravinyltin in a 500-ml. three-necked flask equipped with a condenser, mechanical stirrer and a 250-ml. addi-

(12) R. West and W. Glaze, *ibid.*, **26**, 2096 (1961).

(13) A. N. Nesmeyanov, A. E. Borisov, I. S. Savel'eva and E. I. Goubeva, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1490 (1958).

(14) Analyses were performed by Dr. S. M. Nagy (M.I.T.), by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. Carol Fitz, Needham Heights, Mass. Melting points were taken using a calibrated Fisher-Johns or Mel-Temp melting point apparatus. For most experiments in which ether was used, Mallinckrodt "anhydrous" reagent grade ether was distilled from lithium aluminum hydride before use. Tetrahydrofuran was stored over sodium and distilled from lithium aluminum hydride.

tion funnel with a pressure-equalizing sidearm. The condenser was topped with a nitrogen inlet tube. A white solid precipitated immediately. After the mixture had been stirred for 30 minutes, 32.5 g. (0.1 mole) of tri-*n*-butyltin chloride (Metal & Thermit Corp.), which had been redistilled to give a pure cut of b.p. 97–99° (5 mm.), in 50 ml. of ether was added. The mixture was refluxed for 2 hr. and hydrolyzed with 25 ml. of 5% hydrochloric acid. The solid material was filtered and washed twice with ether. The organic layer was separated, shaken with aqueous potassium hydroxide solution, dried and distilled. After a small forerun, 23.4 g. (74%) of tri-*n*-butylvinyltin was collected at 80–83° (0.6 mm.), n_D^{25} 1.4773; lit.¹⁵ b.p. 114° (3 mm.), n_D^{25} 1.4761.

Anal. Calcd. for $C_{14}H_{30}Sn$: C, 53.03; H, 9.54. Found: C, 53.30; H, 9.25.

The solid material was dried and weighed; 10.3 g. (97%) of crude tetraphenyltin was obtained. Recrystallization from tetrahydrofuran gave solid of m.p. 225–226°. A mixed m.p. with authentic tetraphenyltin showed no depression.

Reaction of Vinylolithium with Triphenylchlorosilane.—A mixture of 4.55 g. (0.02 mole) of tetravinyltin and 85 ml. of 0.94 *M* phenyllithium (0.08 mole) in ether was stirred under nitrogen for 40 min. The mixture was filtered through a sintered glass funnel under nitrogen to remove tetraphenyltin (7.0 g., 82%). To the filtrate was added 20.6 g. (0.07 mole) of triphenylchlorosilane (Dow Corning Corp.). The mixture was refluxed overnight, hydrolyzed and the organic layer separated from the aqueous phase. After removal of the solvent under reduced pressure, the solid residue was crystallized from ethanol to give 10 g. of triphenylvinylsilane, m.p. 66–68°; lit.¹⁶ m.p. 67–68°. Upon concentration of the filtrate, an additional 3.6 g. of product was collected, m.p. 64–66°. The total yield was 68%.

A similar procedure was used in the reaction of vinylolithium with triethylchlorosilane, dimethyldichlorosilane, arsenic trichloride and acetone; the products, triethylvinylsilane, dimethyldivinyldisilane, trivinylarsine and dimethylvinylcarbinol, were isolated by fractional distillation, and their physical constants agreed with those reported for these compounds previously in the literature. The vinylolithium used in the reaction with triphenylgermanium bromide was prepared by the reaction of 0.07 mole of triphenylvinyltin with 0.07 mole of phenyllithium in ether.

Preparation of Solid Vinylolithium and its Reaction in Ether with Triphenylborane.—To 6.8 g. (0.03 mole) of tetravinyltin in a 500-ml. three-necked flask equipped with a mechanical stirrer and nitrogen inlet tube was added 160 ml. of 0.38 *M* *n*-butyllithium (0.06 mole) in pentane. The solution was concentrated by blowing a rapid stream of nitrogen across the surface of the solution. In a short while, vinylolithium began to precipitate. The mixture was concentrated further and then left standing under nitrogen for 10–15 min. The precipitated vinylolithium was filtered under nitrogen, washed twice with pentane and dissolved in ether. The concentration of the resulting solution, determined roughly by a simple acid titration, was 0.38 *M*.

Freshly distilled triphenylborane (4.8 g., 0.02 mole) was dissolved in 150 ml. of ether, and 58 ml. (0.022 mole) of the vinylolithium solution was added. A heavy oil settled to the bottom. The mixture was stirred under nitrogen overnight and the oil drawn off. It appeared stable in methanol solution, even when the solution was left standing in contact with air. A methanolic tetramethylammonium bromide solution was added to a portion of the oil dissolved in methanol. A white solid, tetramethylammonium triphenylvinylboron, precipitated and was filtered, washed with hot methanol and dried. It decomposed slowly above 220°, and decomposition became more rapid above 235° in a sealed tube.

Anal. Calcd. for $C_{24}H_{30}NB$: C, 83.96; H, 8.81. Found: C, 83.97; H, 9.04.

To another portion of the oil dissolved in methanol was added a solution of methyltriphenylphosphonium bromide in the same solvent. A solid precipitated immediately; m.p. 144–150°. Two recrystallizations from methanol

gave white solid, methyltriphenylphosphonium triphenylvinylboron, m.p. 160–161°.

Anal. Calcd. for $C_{39}H_{36}PB$: C, 85.71; H, 6.64. Found: C, 85.70; H, 6.96.

Reaction of Vinylolithium with Boron Trifluoride Etherate.—A solution of vinylolithium in ether was prepared as described in the previous experiment. To 125 ml. of the resulting 0.4 *M* vinylolithium solution (0.05 mole) was added dropwise 0.96 ml. (0.0075 mole) of freshly distilled boron trifluoride etherate dissolved in a small amount of ether. The mixture was refluxed overnight under nitrogen and then filtered to remove the inorganic solids. The ether solution was evaporated under reduced pressure to leave a viscous, ethanol-soluble oil. To a portion of the oil in ethanol was added an ethanolic solution of methyltriphenylphosphonium bromide. Crystals slowly appeared, and after several min. they were filtered. The resulting solid melted at 144–148°. It was recrystallized three times from ethanol to give a white solid, methyltriphenylphosphonium tetravinylboron, m.p. 151–152°.

Anal. Calcd. for $C_{27}H_{30}PB$: C, 81.82; H, 7.63. Found: C, 82.04; H, 7.81.

An ethanolic methyltriphenylarsonium bromide solution was added to a portion of the oil dissolved in ethanol. After about one min. a solid precipitated, m.p. 137–139°. Two recrystallizations from ethanol gave a white solid, methyltriphenylarsonium tetravinylboron, m.p. 142.5–144°.

Anal. Calcd. for $C_{27}H_{30}AsB$: C, 73.66; H, 6.87. Found: C, 73.91; H, 6.85.

Water was added to another portion of the oil in ethanol. The solution became cloudy with noticeable heat evolution.

Carbonation of Vinylolithium.—Dry Ice (*ca.* 700 g.) was crushed and suspended in 200 ml. of ether to which a little hydroquinone had been added. A mixture of 0.375 mole of phenyllithium and 21.3 g. (0.094 mole) of tetravinyltin in ether, which had been stirred for 40 min. at room temperature, was added to the Dry Ice. This mixture was stirred until the excess Dry Ice had evaporated, and then 100 ml. of 3 *M* sulfuric acid was added slowly. The solid was filtered and the organic layer separated from the aqueous phase. The latter was washed twice with methylene dichloride, and the combined organic layers were dried over anhydrous magnesium sulfate. Ether was removed at atmospheric pressure. Fractional distillation of the residue gave 6.3 g. of acrylic acid, b.p. 39° (10 mm.), n_D^{20} 1.4226; lit.¹⁷ b.p. 48° (15 mm.), n_D^{20} 1.4224. The infrared spectrum of this material was identical with the published¹⁸ spectrum of acrylic acid. In addition, 3.7 g. of less pure material, n_D^{20} 1.4255, was obtained at 37–40° (10 mm.). The total yield was 37%. A relatively large amount of viscous residue remained in the distilling flask.

The Stability of Solid Vinylolithium on Aging.—A sample of solid vinylolithium was prepared from 170 ml. of 0.47 *M* *n*-butyllithium in pentane (0.08 mole) and 9.0 g. (0.04 mole) of tetravinyltin. It was filtered under nitrogen, washed with pentane and left standing on the sintered glass filter for 13 days under a nitrogen atmosphere. After this period, ether was added to the solid lithium compound; the entire sample dissolved.

Triphenylchlorosilane (11 g., 0.0375 mole) was added to a 125-ml. aliquot of this solution, which had been determined to be 0.3 *N* in basic lithium. The mixture was refluxed overnight, hydrolyzed, and the organic layer was separated and dried. After removal of the solvent at reduced pressure, the solid residue was distilled at 155–170° (0.3 mm.), and the distillate was crystallized from ethanol to give a total of 7.3 g. of triphenylvinylsilane, m.p. 63–65.5°. This is a yield of 68%.

The Stability of Vinylolithium in Various Solvents.—The stability of vinylolithium in diethyl ether and tetrahydrofuran with time was investigated by determining the yield of tri-*n*-butylvinyltin formed when tri-*n*-butyltin chloride was added to the vinylolithium solutions. The procedure for the reaction has been described above. Solutions of vinylolithium in ether were prepared by the reaction of phenyllithium with tetravinyltin in 4:1 molar ratio. Vinylolithium solutions in tetrahydrofuran were prepared by dissolving solid vinylolithium, obtained from the

(15) S. D. Rosenberg, A. J. Gibbons and H. E. Ramsden, *J. Am. Chem. Soc.*, **79**, 2137 (1957).

(16) L. F. Cason and H. G. Brooks, *ibid.*, **74**, 4582 (1952).

(17) C. Moureu and A. Bontaric, *J. chim. phys.*, **18**, 348 (1920).

(18) American Cyanamid Co., "New Product Bulletin No. 29—Acrylic Acid," 1953.

n-butyllithium-tetravinyltin reaction in pentane, in this solvent. The results are shown in Table II. The tetraphenyltin noted in the last column is that produced in the $\text{PhLi-Vi}_4\text{Sn}$ reaction.

TABLE II
STABILITY OF VINYLITHIUM IN ETHER SOLVENTS

Time ^a	Solvent	Yield (%) of $(\text{C}_6\text{H}_5)_2\text{SnCH=CH}_2$	Yield (%) of $(\text{C}_6\text{H}_5)_4\text{Sn}$
0	Et_2O	65	75
6 min.	Et_2O	65	75
30 min.	Et_2O	74	97
2 hr.	Et_2O	73	
17 hr.	Et_2O	72	
7 days	Et_2O	65	
10 min.	THF	68	
22 hr.	THF	63	
7 days	THF	65	
2.5 hr. (at 65°)	THF	61	

^a Time elapsed between formation of $\text{CH}_2=\text{CHLi}$ and its reaction with tri-*n*-butyltin chloride.

Attempted Preparation of Vinylithium in Tetrahydrofuran.—To 22.6 g. (0.06 mole) of triphenylvinyltin in tetrahydrofuran was added 75 ml. of 0.8 *M* phenyllithium in tetrahydrofuran (0.06 mole). The latter solution was prepared using the method of Gilman and Gaj¹¹ by the reaction of bromobenzene with lithium wire at -60° . The dark red mixture was stirred for two hr. at room temperature; some solid precipitated during this time. Tri-*n*-butyltin chloride (18.5 g., 0.057 mole) was added, and the mixture was stirred for 5 hr. and then hydrolyzed with 5% HCl. Tetraphenyltin (8 g., m.p. 223–225°) was filtered, and the organic layer of the filtrate was distilled to remove solvent. Ether was added to the residue, and the solution was shaken with 35 g. of potassium hydroxide in 150 ml. of water. The ether layer was separated, the solvent removed and an additional 1.5 g. of tetraphenyltin was filtered (total yield 39%).

Distillation of the filtrate gave no tri-*n*-butylvinyltin. Crude tri-*n*-butylphenyltin was distilled between 115–130° (0.25–0.45 mm.). This was redistilled to give 6.8 g. (33%) of tri-*n*-butylphenyltin, b.p. 116–118° (0.25 mm.), n_D^{20} 1.5169; lit.¹⁹ b.p. 139° (0.6 mm.), n_D^{20} 1.5155. The residue was distilled to obtain any higher boiling products, but only decomposition resulted.

Reaction of Vinylithium with Tetraphenyltin in Tetrahydrofuran.—Solid vinylithium was prepared by adding 0.1 mole of *n*-butyllithium in pentane to 0.05 mole of tetraphenyltin and was dissolved in tetrahydrofuran. Tetraphenyltin (21.3 g., 0.05 mole) was dissolved in 500 ml. of hot tetrahydrofuran, and this solution was cooled to room temperature. A large amount of tetraphenyltin precipitated on cooling. To this mixture was added 100 ml. of the yellow vinylithium solution (determined to be 0.5 *M*) in tetrahydrofuran. The precipitated tetraphenyltin immediately dissolved. After 10 min., the color of the solution changed to red, the color characteristic of phenyllithium in tetrahydrofuran. Addition of 150 ml. of water caused precipitation of 9 g. of tetraphenyltin, m.p. 223–225°, which was filtered off. Separation of the organic layer and removal of the solvent gave another 1.3 g. of tetraphenyltin (total recovery 49%). Attempted distillation of the liquid residue was not successful.

In another experiment, 17.3 g. of tetraphenyltin was dissolved in 600 ml. of hot tetrahydrofuran (the total volume of solvent present in the previous experiment), and on cooling to room temperature, 6.7 g. precipitated. Thus the solubility of tetraphenyltin in dry tetrahydrofuran is ca. 10.5 g. in 600 ml. at room temperature. This supports the belief that in the previous experiment vinylithium and tetraphenyltin had reacted in an as yet unknown manner.

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(19) H. Gilman and S. D. Rosenberg, *J. Am. Chem. Soc.*, **75** 2507 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IOWA, IOWA CITY, IOWA]

Studies on the Chemistry of Halogens and of Polyhalides. XXI. Halogen Complexes of 4,4'-Bipyridine and the Infrared Spectra of Pyridine Complexes

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The preparation of solid 1:2 addition compounds of 4,4'-bipyridine with iodine halides is described. These compounds, in contrast with the analogous 2,2'-bipyridine complexes, are insoluble in common organic solvents, polar as well as non-polar. This precludes the possibility of studying them in solutions. Since unipositive iodine can have a coordination number of two, the properties of these complexes may indicate that these are linear polymers of the type $\dots \text{BP-I}^+-\text{BP-I}^+-\text{BP-I}^+ \dots$ with an equivalent number of IX_2^- ions attached electrostatically to the chain. Infrared spectra of these complexes as well as those of pyridine and 2,2'-bipyridine with iodine monochloride and with silver ion were observed in the 300–4000 cm^{-1} spectral region. In view of the complexity of these spectra only qualitative comparisons are given.

Introduction

While numerous halogen complexes of simple heterocyclic amines have been studied in the past, very little attention has been paid to the complexes of polynuclear heterocycles. A recent study of the 2,2'-bipyridine-iodine halide complexes gave some indications that the positive iodine may be coordinated to two nitrogen atoms of the bipyridine with the molecule being arranged in the *cis* configuration.² Since such an arrangement is obvi-

ously impossible in the case of 4,4'-bipyridine, it was of interest to study the properties of the corresponding halogen complexes. A comparison was made between infrared spectra of the halogen and of the silver complexes.

References to complexes of 4,4'-bipyridine are not plentiful in the literature. The two most pertinent reports describe the formation of complexes with arsenic tribromide³ and silver nitrate.⁴ In both cases evidence is cited indicating that the two addition compounds are polymeric, with a

(1) Department of Chemistry, Northern Illinois University, DeKalb, Illinois.

(2) A. I. Popov and R. T. Pfau, *J. Am. Chem. Soc.*, **79**, 570 (1957).

(3) P. Popov, *Zhur. Obshchei Khimii*, **19**, 47 (1947).

(4) W. J. Peard and R. T. Pfau, *J. Am. Chem. Soc.*, **80**, 1593 (1958).