AD-A090 013 OKLAHOMA UNIV NORMAN DEPT OF CHEMISTRY F/G 7/3
SYNTHESIS OF TETRAPHENYLSTRANNACY-CLOPENTADIENES (STANNOLES). I--ETC(U)
OCT 80 W - RHEE, J J ZUCKERMAN N00014-77-C-0432
UNCLASSIFIED TR-22 NL

1 of 1
AD
A090013

END
DATE
FILMED
10 80
DTIC

(12)

OFFICE OF NAVAL RESEARCH

Contract N00014-77-C-0432

Task No. NR 053-639

TECHNICAL REPORT NO. 22

TR-

Synthesis of Tetraphenylstrannacyclopentadienes (Stannoles). III. Attempted Route to the Parent Stannoles Through Closure of 1,4-Dichlorobuta-1,3-diene[1]

by

W. -Z. Min Rhee ~~and~~ J. J. Zuckerman

Prepared for Publication

in

The Journal of Organometallic Chemistry

1 Oct 79

19

University of Oklahoma
Department of Chemistry
Norman, Oklahoma 73019

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

410 717

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER 22	2. GOVT ACCESSION NO. AD-A090 013	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Synthesis of Tetraphenylstannacyclopentadienes (Stannoles). III. Attempted Route to the Parent Stannoles Through Closure of 1,4-Dichlorobuta-1,3-diene		5. TYPE OF REPORT & PERIOD COVERE 6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) W.-Z. Min Rhee and J. J. Zuckerman		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0432
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Oklahoma Department of Chemistry Norman, Oklahoma 73019		10. PROGRAM ELEMENT, PROJECT, TA AREA & WORK UNIT NUMBERS NR 053-636
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		12. REPORT DATE 1 October, 1980 13. NUMBER OF PAGES 8
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release, Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in the Journal of Organometallic Chemistry

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Organotin derivatives, Tetraorganotins, Infrared, Nuclear magnetic resonance, Mössbauer spectroscopy, Mass spectroscopy, Tin-119m Mössbauer spectroscopy, Metalloles, Stannoles, Siloles, 1,4-Dichlorobuta-1,3-diene, Lithiation, Organochlorosilanes, Organotin chlorides, Dehydrochlorination, Multiple bond migration, 1,4-Bis(trimethylsilyl)buta-1,3-diyne, 1,4-Bis(trimethyltin)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

1,4-Dichlorobuta-1,3-diene has been lithiated and reacted with organosilyl and tin chlorides. Only polymerized starting material, rather than the hoped for parent sila- and stannacyclopentadienyl (silole and stannole) ring systems result from the action of the lithiated material on diorganodichlorosilanes and diorganotin dichlorides. Addition of the lithiated butadiene to trimethylchlorosilane and trimethyltin chloride yields products resulting from dehydrochlorination and multiple bond migration in the starting dichlorobutadiene.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data En

19. butatriene, Poly-1,4-dichlorobutadiene.

Synthesis of Tetraphenylstannacyclopentadienes (Stannoles). III. Attempted Route to the Parent Stannoles Through Closure of 1,4-Dichlorobuta-1,3-diene[1]

W.-Z. Min Rhee and J. J. Zuckerman*

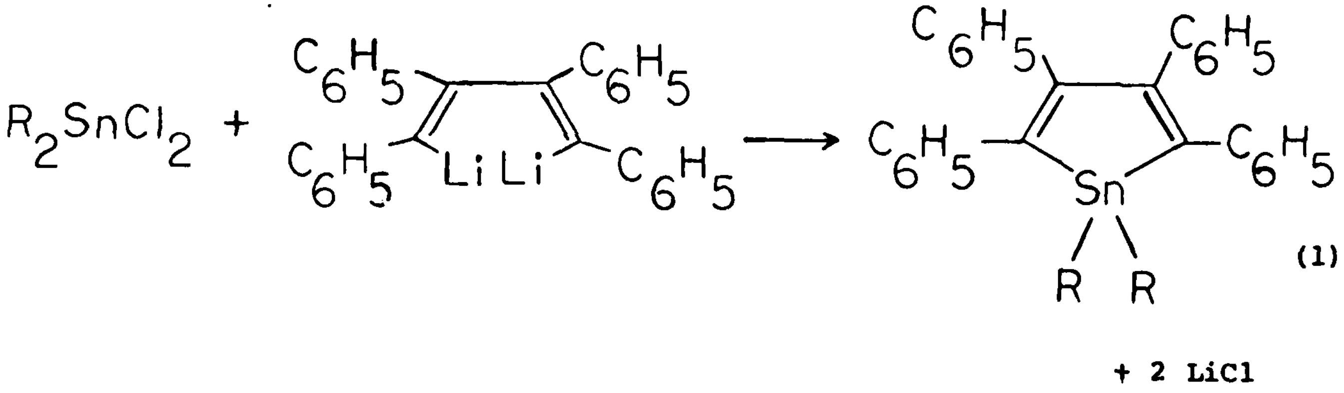
Department of Chemistry
University of Oklahoma
Norman, OK 73019

Summary

1,4-Dichlorobuta-1,3-diene has been lithiated and reacted with organosilyl and tin chlorides. Only polymerized starting material, rather than the hoped for parent sila- and stannacyclopentadienyl (silole and stannole) ring systems result from the action of the lithiated material on diorganodichlorosilanes and diorganotin dichlorides. Addition of the lithiated butadiene to trimethylchlorosilane and trimethyltin chloride yields products resulting from dehydrochlorination and multiple bond migration in the starting dichlorobutadiene.

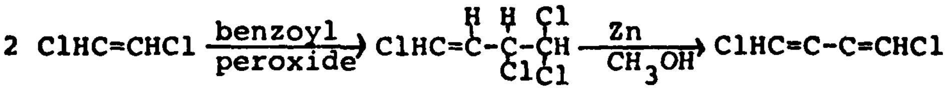
Variously 1,1-disubstituted stannoles based upon the 2,3,4,5-tetraphenylstannacyclopentadiene system have been synthesized and reported as part of this series of papers.[1-2] The parent stannole ring system is, however, unknown.

One possible approach is through the 1,4-dilithio derivative of the unsubstituted butadiene-1,3 by analogy with the now well-known and general reaction of the <u>cis</u>-,<u>cis</u>-1,4-dilithio-1,2,3,4-tetraphenylbutadiene with organometallic and metalloidal dihalides. The reaction of diorganotin dihalides, for example, affords a convenient route to the stannoles:[3-6]



(1)

The dihalo- precursor to the simple dilithio compound, 1,4-dichlorobuta-1,3-diene, can be prepared by the dimerization of 1,2-dichloroethylene with benzoyl peroxide and dechlorination of the resulting 1,3,4,4-tetrachlorobutene-1 by metallic zinc dust in methanol:[7-10]

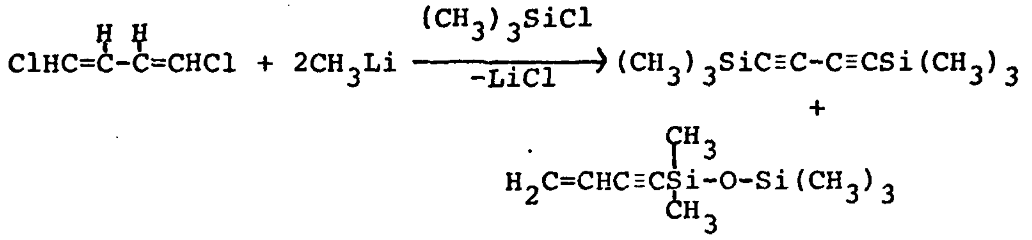


$$2\ \mathrm{ClHC{=}CHCl} \xrightarrow[\text{peroxide}]{\text{benzoyl}} \mathrm{ClHC{=}\overset{H}{C}{-}\underset{Cl}{\overset{H}{C}}{-}\underset{Cl}{\overset{Cl}{C}}H} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{Zn}} \mathrm{ClHC{=}C{-}C{=}CHCl} \qquad (2)$$

The infrared spectrum of the product showed the superimposition of bands arising from the *cis*-,*cis*-; *cis*-,*trans*- and *trans*-,*trans*-isomers of 1,4-dichlorobuta-1,3-diene.[7] The mass spectrum contained the parent ion as a polyisotopic peak at m/e = 126.

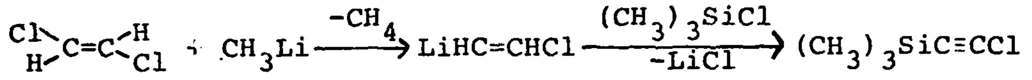
Unfortunately, treatment of the 1,4-dichlorobutadiene with conventional lithiating agents followed by addition of either diorganodichlorosilanes or diorganotin dichlorides results only in the polymerization of the starting material. The infusible white solid polymer leaves no silicon or tin(IV) oxide residue on burning, and exhibits in its infrared spectrum absorption bands at 1638 cm^{-1} arising from a -C=C- stretching mode, a second at 842 cm^{-1} which can be assigned to a δ(C-H) out-of-plane deformation mode and a broad band centered at 650 cm^{-1} from a ν(C-Cl) mode. Carbonylation of the expected 1,4-dilithio intermediate did not give an unambiguous 1,4-dicarboxylic acid product on hydrolysis. Neither did reaction of trimethylchlorosilane or trimethyltin chloride give the expected 1,4-bis(trimethylmetalloidal) derivatives.

Addition of the 1,4-dichlorobutadiene lithiated by methyllithium to a solution of trimethylchlorosilane in ether gave a precipitate and a filtrate from which two silicon-containing products could be isolated, 1,4-bis(trimethylsilyl)buta-1,3-diyne, and what appears to be a trace of a hydrolysis or oxidation product from 1-trimethylsilylbuta-1-yne-3-ene which results during glc separation and collection:



$$\mathrm{ClHC{=}\overset{H}{C}{-}\overset{H}{C}{=}CHCl} + 2\mathrm{CH_3Li} \xrightarrow[-\mathrm{LiCl}]{(\mathrm{CH_3})_3\mathrm{SiCl}} (\mathrm{CH_3})_3\mathrm{SiC{\equiv}C{-}C{\equiv}CSi(CH_3)_3} + \mathrm{H_2C{=}CHC{\equiv}C\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}Si(CH_3)_3} \qquad (3)$$

The 1,4-bis-(trimethylsilyl)buta-1,3-diyne is similar to the product of the treatment of 1,2-dichloroethylene with methyllithium followed by trimethylchlorosilane to give 1-trimethylsilyl-2-chloroacetylene:[11]



$${}^{\mathrm{Cl}}_{\mathrm{H}}{>}\mathrm{C{=}C}{<}^{\mathrm{H}}_{\mathrm{Cl}} + \mathrm{CH_3Li} \xrightarrow{-\mathrm{CH_4}} \mathrm{LiHC{=}CHCl} \xrightarrow[-\mathrm{LiCl}]{(\mathrm{CH_3})_3\mathrm{SiCl}} (\mathrm{CH_3})_3\mathrm{SiC{\equiv}CCl} \qquad (4)$$

1,4-Bis(trimethylsilyl)butadiyne-1,3 has been synthesized by the dimerization of ethynyltrimethylsilane by the copper(I) chloride tetramethylethylenediamine complex in the presence of oxygen gas.[12,13]

Analogous reaction of the lithiated 1,4-dichlorobutadiene with trimethyltin chloride gave only one tin-containing product, 1,4-bis-(trimethyltin)butatriene, along with a large yield of the polymerized 1,4-dichlorobutadiene.

$$\mathrm{ClHC{=}C{-}C{=}CHCl} + 2\mathrm{CH_3Li} \xrightarrow[-\mathrm{LiCl}]{(\mathrm{CH_3})_3\mathrm{SnCl}} (\mathrm{CH_3})_3\mathrm{SnC{=}C{=}C{=}CSn(CH_3)_3} \qquad (5)$$

Thus both the silicon and tin reactions result in products which derive from dehydrochlorination and multiple bond migration in the starting 1,4-dichlorobutadiene.

Experimental

1,3,4,4-Tetrachloro-1-butene

1,2-Dichloroethylene (430 g cis- and trans-mixture, b.p. 56-62°) was allowed to reflux for 14 days with dibenzoyl peroxide (4.5 g, mmoles). After the removal of unreacted starting material, distillation gave the following fractions: b.p. 40-85.2° (18.5 mm), 10 g; b.p. 84.2-94.0° (18.5 mm), 160 g and b.p. 94.0-94.3° (18.5 mm), 1 g.

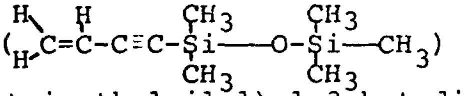
Dechlorination

A solution of 1,3,4,4-tetrachloro-1-butene (140 g, second fraction, 0.73 mol) in methanol (140 mL) was added dropwise in the course of 105 min to a stirred suspension of zinc dust (315 g, 4.82 g-atoms) in methanol (420 mL). Toward the end of the addition the mixture was allowed to reflux gently. After stirring 24 hr at room temperature the hydrochloric acid solution was extracted with methylene chloride. Drying and evaporation of the organic solvent gave an oil which on distillation gave the following fractions: b.p. 29.5-37.0° (15-25 mm), 8.0 g; b.p. 31.5-35.0° (16.5 mm), 60.0 g and b.p. 35.0-60.0° (16.5 mm), 5.2 g. The total yield was 73.2 g (82% of theory).

The infrared spectrum showed bands at 3085(s), 3065(s), 1755(m,b), 1702(m,b), 1671(m,b), 1623(s), 1568(s), 1355(m), 1336(s), 1304(s,d), 1240(w), 1184(m,d), 1115(m), 1092(m), 950(s,sh), 910(m), 845(s), 805(s,sh), 765(s,b), 710(s), 598(m) and 495(m) cm^{-1}. The mass spectrum contained fragments up to m/e = 126 which is the molecular ion. An abundant peak appeared at m/e = 122.

Reaction of Lithiated 1,4-Dichloro-1,3-butadiene with Trimethylchlorosilane

Methyllithium in ethyl ether (8.00 mL, 13.36 mmoles) was added dropwise to an ether solution of 1,4-dichloro-1,3-butadiene (2 g, 16.3 mmoles). The reaction was cooled in a Dry Ice/acetone bath under nitrogen and the temperature slowly raised to ambient. The brown-colored solution gave a brown-white colored suspension after stirring at room temperature for 2 hours. The lithium solution was added dropwise at -70° to a solution of trimethylchlorosilane (4.1 ml, 31.99 mmoles) in ethyl ether (5 mL), and the temperature slowly raised to ambient. Refluxing 30 minutes gave a tan colored precipitate for which the infrared spectrum lacked the stretching frequency associated with the $Si-(CH_3)_3$ group at 750 cm^{-1}.

After the removal of the solvent, the filtrate was distilled to give the following fractions: b.p. 30.5-42.5 (16.5 mm), 1.1 g (1,4-dichloro-1,3-butadiene); b.p. 75-78.0 (15 mm), 0.3 g ( $H_2C=C(H)-C\equiv C-Si(CH_3)_2-O-Si(CH_3)_2-CH_3$) and b.p. 90-92.5 (10 mm), 0.9 g [1,4-bis trimethylsilyl)-1,3-butadiyne].

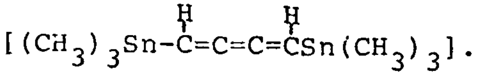
The third fraction collected at 90-92.5° (10 mm) was found to be 1,4-trimethylsilyl-1,3-butadiyne (mp = 107°; lit.[12-13] = 107°). The infrared spectrum showed bands at 2960(s), 2900(m), 2065(s,sh), 1413(m), 1250(s), 850(s,b), 765(s), 708(m), 650(s), 557(s), 470(w) and 382(s) cm^{-1}. The nmr spectrum in $CDCl_3$ contained only a singlet at 0.76 ppm (lit.[12]=9.85 ppm) for the trimethylsilyl protons.

The second fraction was separated and collected by gas chromatography [6 ft. column, 10% UC-W98 (silicone oil) 80-100 packing on Chromosorb W]. The infrared spectrum of the second fraction in

$CDCl_3$ contained two singlets at 9.82 and 9.86 in addition to the vinyl group proton multiplet. The proton integration ratio was found to be 1:4.4 = vinyl:methyl vs. the calculated ratio of 1:5. The mass spectrum of this fraction contained fragments up to m/e = 194. An abundant silicon-containing fragment appeared at m/e (^{28}Si) = 143 and a less abundant fragment at m/e = 117. Anal. Calcd. for $C_9H_{18}Si_2O$: C, 54.58; H, 9.14. Found: C, 53.27; H, 7.12%.

Reaction of Lithiated 1,4-Dichloro-1,3,butadiene with Trimethyltin Chloride

Into a solution of trimethyltin chloride (6.26 g, 31.99 mmoles) in ethyl ether (5 mL) the lithium reagent (13.36 mmoles) prepared as above was added dropwise at -70° and the temperature slowly raised to ambient. Refluxing for 30 minutes gave white-brown colored precipitate, for which the infrared spectrum lacked the stretching frequency of the $Sn(CH_3)_3$ group at 556 cm^{-1}.

After the removal of the solvent, the filtrate was distilled to give the following fractions: b.p. 30.5-42.5 (16.5 mm), 1.2 g (1,4-dichloro-1,3-butadiene) and b.p. 55.0-58.8 (18.0 mm), 1.5 g (24.8% yield)  $[(CH_3)_3Sn-\overset{H}{C}=C=C=\overset{H}{C}Sn(CH_3)_3]$.

The infrared spectrum of the latter contained bands at 3060(w,sh), 2998(m), 2920(m), 2375(w), 1759(w), 1715(w), 1623(w), 1569(m), 1400(w,b), 1335(w), 1300(w,d), 1194(m), 1120(w), 1092(w), 950(m,sh), 840(m), 790(s,b), 550(s), 515(w) and 325(s,b) cm^{-1}. The nmr spectrum in $CDCl_3$ contained a singlet at 9.31 ppm with $|^2J(^{119}Sn-C-^1H)|$ = 56.1 Hz. In addition, the portionintegration ratio was found to be 1:9 = vinyl:methyl vs. 1:9 calcd.

Acknowledgement

Our work is supported by the Office of Naval Research and by the National Science Foundation through Grant CHE-78-26548. We thank M&T Chemicals, Inc. for the donation of organotin starting materials.

References

(1) For Part II of this series see: W. A. Gustavson, L. M. Principe, W.-Z. Min Rhee and J. J. Zuckerman, submitted for publication.

(2) W. A. Gustavson, L. M. Principe, W.-Z. Min Rhee and J. J. Zuckerman, submitted for publication.

(3) F. C. Leavitt, T. A. Manuel, F. Johnson, L. U. Matternas and S. Lehman, J. Am. Chem. Soc., 82(1960) 5099.

(4) E. H. Braye, W. Hubel and I. Caplier, J. Am. Chem. Soc., 83(1961) 4406.

(5) H. H. Freeman, J. Org. Chem. 27(1962) 2298.

(6) J. G. Zavistoski and J. J. Zuckerman, J. Org. Chem., 34(1969) 4197.

(7) P. D. Bartlett and G. E. H. Wallbillich, J. Am. Chem. Soc., 55(1969) 409.

(8) H. G. Viele and E. Franchimont, Chem. Ber., 97(1964) 602.

(9) R. Criegee, W. Horauf and W. D. Schellenberg, Chem. Ber., 86(1953) 126.

(10) W. Bauer, Chimia, 5(1951) 147.

(11) W. Steingross and W. Zeil, J. Organomet. Chem., 6(1966) 109.

(12) D. M. Walton and F. Waugh, J. Organomet. Chem., 37(1972) 45.

(13) I. A. Shikhiev, M. F. Shostakovskii and L. A. Kayutenko, Dokl. Akad. Nauk Azerb. SSR, 15(1959) 21.