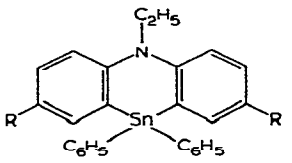
*Journal of Organometallic Chemistry*
Elsevier Publishing Company Amsterdam
Printed in The Netherlands



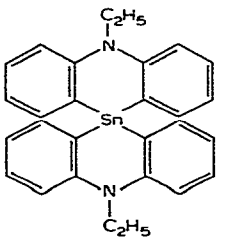
## SHORT COMMUNICATION

### Some new 5,10-dihydrophenazastannine derivatives. The novel conversion of 5,10,10-trimethyl-5,10-dihydrophenazastannines into their phosphorus(III) analogs

Only three 5,10-dihydrophenazastannine derivatives (I), (II), and (III) have previously been reported. They were prepared by allowing the 2,2′-dilithio derivative




(I) (R=H)
(II) (R=Br)




(III)

of the appropriate N-ethyl-2,2′-dibromodiphenylamine to react with diphenyltin dichloride or stannic chloride. We have used this synthetic method to prepare [except for (X)] the compounds in Tables 1 and 2, and we wish to report on some of their chemical transformations.

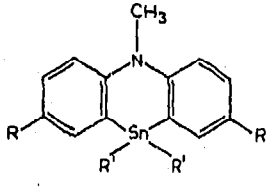
It was found that (VIII) and (XIII) could be converted into (X) by reaction with stannic chloride in refluxing xylene (63% and 68% yield, respectively). With (XIII), only (X) was obtained, whereas with (VIII), dimethyltin dichloride (46% yield) was also obtained. These reactions are not unexpected since it is well known that stannic chloride reacts with compounds of the type $R_4Sn$ to give compounds of the type $R_2SnCl_2$[3]. Furthermore, this reaction has been employed in the tin heterocycle field by Kuivila and Beumel[4]. The preparation of (X) enabled the synthesis of compounds (VIII) and (IX) by another route. The reaction of (X) with methylmagnesium bromide or methyllithium gave (VIII) (75% and 47% yield, respectively). The reaction of (X) with phenylmagnesium bromide or phenyllithium gave (IX) (92% and 47% yield, respectively).

The reaction of (VIII) with stannic chloride to give (X) and dimethyltin dichloride suggested that compounds (IV), (VI), and (VIII) might be converted into heterocyclic analogs by reaction with compounds containing bonds which are known to cleave $R_4Sn$ compounds to give organotin halides. Recently, the conversion of cyclic esters of silicon into their phosphorus(III) and phosphorus(V) analogs in one step[5] and the conversion of silicon and germanium imidazolidines into their phosphorus(V) analogs in one step[6] were described. The ability of phosphorus(III) bromide to cleave $R_4Sn$ compounds[7] suggested that compounds (IV), (VI), and (VIII) might be converted into their phosphorus(III) analogs by reaction with phenyldichlorophosphine. This was found to be the case. The reaction of (IV) with phenyldi-

J. Organometal. Chem., 10 (1967) 181–187

TABLE 1

5-METHYL-10,10-DIORGANO-5,10-DIHYDROPHENAZASTANNINES

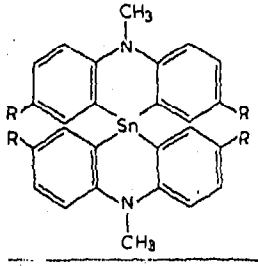



| *No.* | *R* | *R'* | *M.p.* (°C) | *Yield* (%) | *Calcd.* (%) | | | | *Found* (%) | | | | *Mol.wt.* | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | *C* | *H* | *N* | *Sn* | *C* | *H* | *N* | *Sn* | *Calcd.* | *Found* | |
| | | | | | | | | | | | | | | *Rast* | *Thermoelectric*[a] |
| (IV) | H | $CH_3$ | 133–134[b] | 51 | 54.59 | 5.19 | 4.25 | 35.97 | 54.64 | 5.27 | 4.32 | 35.24 | 329.99 | 326 | 301 |
| (V) | H | $C_6H_5$ | 148.5–150[c] | 52 | 66.12 | 4.66 | 3.09 | 26.14 | 66.03 | 4.39 | 3.35 | 25.51 | 454.13 | 432 | 359 |
| (VI) | $CH_3$ | $CH_3$ | 119–120[b] | 63 | 57.02 | 5.91 | 3.91 | 33.15 | 57.01 | 6.10 | 3.82 | 33.05 | 358.05 | 354 | 323 |
| (VII) | $CH_3$ | $C_6H_5$ | 146–148[d] | 34 | 67.25 | 5.23 | 2.91 | 24.62 | 67.11 | 5.33 | 2.91 | 24.26 | 482.18 | 366 | 404 |
| (VIII) | Br | $CH_3$ | 122–123[d] | 73 | 36.93 | 3.10 | 2.87 | 24.33 | 36.93 | 2.90 | 3.16 | 23.23 | 487.80 | 498 | 502 |
| (IX) | Br | $C_6H_5$ | 191–193[e] | 26 | 49.07 | 3.13 | 2.29 | 19.40 | 49.23 | 3.29 | 2.36 | 18.97 | 611.90 | [f] | 600 |
| (X) | Br | Cl | 164.5–166.5[g] | 63[h], 68[i] | 29.54 | 1.72 | 2.65 | 22.45 | 29.66 | 1.71 | 2.83 | 21.79 | 528.67 | [f] | 782 |

[a] Determined in 2-butanone. [b] Recryst. from n-hexane/ethyl acetate. [c] Recryst. from ethyl acetate. [d] Recryst. from n-hexane. [e] Recryst. from n-hexane/diethyl ether. [f] Not determined. [g] Recryst. from benzene/petroleum ether (b.p. 30–60°). [h] From (VIII) and stannic chloride. [i] From (XIII) and stannic chloride.

TABLE 2

5,5′-DIMETHYL-10,10′-SPIROBI(5,10-DIHYDROPHENAZASTANNINE)S




| No. | R | M.p. (°C) | Yield (%) | Calcd. (%) | | | | Found (%) | | | | Mol. wt. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | Sn | C | H | N | Sn | Calcd. | Found | |
| | | | | | | | | | | | | | Rast | Thermoelectric[a] |
| (XI) | H | 164–166[b] | 49 | 64.90 | 4.61 | 5.82 | 24.67 | 64.82 | 4.82 | 5.66 | 23.39 | 481.15 | 360 | [c] |
| (XII) | $CH_3$ | 209–211[d] | 78 | 67.06 | 5.63 | 5.22 | 22.09 | 67.23 | 5.60 | 5.29 | 22.19 | 537.26 | 527 | 468 |
| (XIII) | Br | 259–260[e] | 77 | 39.19 | 2.28 | 3.52 | 14.89 | 39.32 | 2.12 | 3.48 | 14.45 | 796.78 | 780 | 800 |

[a] Determined in 2-butanone. [b] Recryst. from n-hexane/methylene chloride. [c] Not determined because of insolubility. [d] Recryst. from n-hexane. [e] Recrystallized from ethyl acetate.

chlorophosphine at 180–210° gave the known compounds, dimethyltin dichloride and 5-methyl-10-phenyl-5,10-dihydrophenophosphazine (59% yield). The latter compound was originally prepared by allowing phenyldichlorophosphine to react with N-methyl-2,2′-dilithiodiphenylamine[8]. Similarly, (VI) and (VIII) gave the new compounds, 2,5,8-trimethyl-10-phenyl-5,10-dihydrophenophosphazine (36% yield) and 2,8-dibromo-5-methyl-10-phenyl-5,10-dihydrophenophosphazine (55% yield), respectively. The latter two compounds were identical in every respect to samples obtained by allowing phenyldichlorophosphine to react with the appropriate N-methyl-2,2′-dilithiodiphenylamine.

Infrared, far infrared, ultraviolet, and NMR data for all of the new compounds are presented in the experimental section.

*Experimental*

Melting points were determined with a Mel-Temp capillary melting point apparatus and are uncorrected. All reactions were carried out in an atmosphere of prepurified nitrogen. Elemental analyses and Rast molecular weight determinations were performed by Dr. G. Weiler and Dr. F. Strauss, Microanalytical Laboratory, Oxford, England. Tin analyses and thermoelectric molecular weight determinations (carried out at 37° by the method of Tomlinson[9]) were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, N.Y. The infrared data were obtained using KBr pellets with a Beckman IR 8 infrared spectrophotometer. The far-infrared date were obtained using KBr pellets with a Perkin–Elmer Model 21 double beam infrared spectrophotometer which was fitted with a cesium bromide prism and purged with nitrogen. The ultraviolet data were obtained with a Bausch and Lomb Spectronic 505 spectrophotometer using chloroform as solvent. The NMR spectra were determined with a Varian Model A-60 NMR spectrometer using deuteriochloroform as solvent and tetramethylsilane as the internal standard. Except for (X), the procedure for preparing the compounds in Tables 1 and 2 was essentially the same as that described in detail for (IV).

5,10,10-*Trimethyl*-5,10-*dihydrophenazastannine* (*IV*). To a solution of 10.0 g (0.0293 mole) of N-methyl-2,2′-dibromodiphenylamine[8,10] in 100 ml of diethyl ether at 0° was added a n-hexane solution of n-butyllithium (86 ml, 0.059 mole), and the mixture was stirred at 0° for 1 h after which 6.27 g (0.0293 mole) of dimethyltin dichloride in 50 ml of diethyl ether was added. The mixture was stirred at 25° for 24 h after which the solvent was removed *in vacuo*, toluene (200 ml) was added, and the mixture was refluxed for 4 h after which it was poured into ice/water. The organic layer was separated, and the water layer was extracted with two 50-ml portions of diethyl ether. Hydroquinone (500 mg) was added to the combined organic layers which were dried and then distilled *in vacuo* leaving an oil which afforded upon recrystallization from ethyl acetate 4.17 g (48%) of (IV), m.p. 129–132°. Repeated recrystallizations from n-hexane/ethyl acetate gave the analytical sample, m.p. 133–134°; IR: 12.99 $\mu$ (1,2-disubstitution); far IR: 16.45, 17.25, 18.60, 19.15, 22.39, and 25.08 $\mu$; NMR: $\tau$ 9.53 [$Sn(CH_3)_2$], 6.60 (singlet, $NCH_3$) and 2.5–3.2 (multiplet, aromatic CH); ratio of aliphatic/aromatic protons, 1.23 (theoretical, 1.13); UV: 242 m$\mu$ ($\varepsilon$ 6770) and 283 m$\mu$ ($\varepsilon$ 10,100).

In another run the yield was 51%.

(*V*). IR: 13.03 and 14.31 $\mu$ (1,2-disubstitution, monosubstitution); far IR: 16.54,

17.34, 19.64, 22.46, and 25.64 $\mu$; NMR: $\tau$ 6.59 (singlet, $NCH_3$) and 2.2–3.1 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 5.82 (theoretical, 6.0); UV: 243 m$\mu$ ($\varepsilon$ 7280) and 284 m$\mu$ ($\varepsilon$ 10,200).

(*VI*). IR: 11.40 and 12.12 $\mu$ (1,2,4-trisubstitution); far IR: 15.39, 17.44, 18.79, 19.24, 22.28, 23.93, 25.17, 28.82, and 29.90 $\mu$; NMR: $\tau$ 9.55 [$Sn(CH_3)_2$], 7.73 (singlet, $CCH_3$), 6.66 (singlet, $NCH_3$), and 2.7–3.0 (multiplet, aromatic CH); ratio of aliphatic/aromatic protons, 2.47 (theoretical, 2.5); UV: 240 m$\mu$ ($\varepsilon$ 5600), 280 m$\mu$ ($\varepsilon$ 7930), and 320 m$\mu$ ($\varepsilon$ 2560).

(*VII*). IR: 11.30 and 12.14 $\mu$ (1,2,4-trisubstitution) and 14.32 $\mu$ (monosubstitution); far IR: 15.24, 17.39, 19.39, 22.98, 23.53, and 29.72 $\mu$; NMR: $\tau$ 7.79 (singlet, $CCH_3$), 6.65 (singlet, $NCH_3$), and 2.3–3.2 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 1.94 (theoretical, 1.78); UV: 244 m$\mu$ ($\varepsilon$ 7300), 283 m$\mu$ ($\varepsilon$ 9510), and 325 m$\mu$ ($\varepsilon$ 3100).

(*VIII*). IR: 11.35 and 12.19 $\mu$ (1,2,4-trisubstitution); far IR: 15.67, 17.34, 18.80, 19.31, 20.88, and 22.33 $\mu$; NMR: $\tau$ 9.53 [$Sn(CH_3)_2$], 6.70 (singlet, $NCH_3$), and 2.5–3.2 (multiplet, aromatic CH); ratio of aliphatic/aromatic protons, 1.41 (theoretical, 1.50); UV: 243 m$\mu$ ($\varepsilon$ 7810) and 290 m$\mu$ ($\varepsilon$ 16,200).

(*IX*). IR: 11.20 and 12.20 $\mu$ (1,2,4-trisubstitution) and 14.34 $\mu$ (monosubstitution); far IR: 15.37, 15.70, 17.36, 19.28, 21.12, 22.37, 22.80, and 23.21 $\mu$; NMR: $\tau$ 6.67 (singlet, $NCH_3$) and 2.4–3.0 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 5.50 (theoretical, 5.33); UV: 243 m$\mu$ ($\varepsilon$ 19,400) and 290 m$\mu$ ($\varepsilon$ 24,500).

2,8-*Dibromo*-5-*methyl*-10,10-*dichlorophenazastannine* (*X*). *From* (*XIII*) *and stannic chloride.* A mixture of (XIII) (20.0 g, 0.025 mole), stannic chloride (6.54 g, 0.025 mole), and *p*-xylene (25 ml) was refluxed for 3 h after which the *p*-xylene was removed *in vacuo*, and the residue was extracted with benzene. The benzene solution was concentrated, and the solid which separated was removed by filtration and discarded. Petroleum ether (b.p. 30–60°) was slowly added to the hot filtrate, and the crystals which separated were collected on a filter to give 16.6 g of solid, m.p. 166–169°. Recrystallization from benzene/petroleum ether (b.p. 30–60°) gave 15.0 g (57%) of (X), m.p. 165–167°. Repeated recrystallizations from benzene/petroleum ether (b.p. 30–60°) gave the analytical sample, m.p. 164.5–166.5°; IR: 11.47 and 12.13 $\mu$ (1,2,4-trisubstitution); far IR: 15.61, 17.36, 19.38, 21.18, 22.97, 27.12, and 28.05 $\mu$; NMR: $\tau$ 6.60 (singlet, $NCH_3$) and 2.2–3.0 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 2.12 (theoretical, 2.0); UV: 243 m$\mu$ ($\varepsilon$ 14,500), 283 m$\mu$ ($\varepsilon$ 18,500) and 350 m$\mu$ ($\varepsilon$ 5820). In another run the yield was 68%.

*From* (*VIII*) *and stannic chloride.* A mixture of (VIII) (4.0 g, 0.0082 mole), stannic chloride (2.13 g, 0.0082 mole), and *p*-xylene (10 ml) was refluxed for 3 h after which the *p*-xylene was distilled *in vacuo*. The oil bath temperature was then raised to 195°, and the residue was distilled *in vacuo* to give 0.87 g (46%) of dimethyltin dichloride, m.p. 104–106°, no depression on admixture with an authentic sample, infrared spectrum superimposable on that of an authentic sample.

The residue was extracted with 50 ml of benzene, petroleum ether (b.p. 30–60°) was added, and the solution was cooled to give 2.72 g (63%) of (X), m.p. 163–165°, no depression on admixture with a sample obtained from XIII.

(*XI*). IR: 13.00 $\mu$ (1,2-disubstitution); far IR: 15.15, 16.55, 17.35, 19.30, 19.75, 22.64, and 25.33 $\mu$; NMR: $\tau$ 6.45 (singlet, $NCH_3$) and 2.5–3.0 (multiplet, aromatic CH): ratio of aromatic/aliphatic protons, 2.85 (theoretical, 2.68); UV: 243 m$\mu$ ($\varepsilon$

9140), 285 mμ (ε 12,000), and 324 mμ (ε 4970).

(*XII*). IR: 11.32 and 12.24 μ (1,2,4-trisubstitution); far IR: 15.39, 17.44, 18.34, 19.39, 22.43, 27.17, and 29.17 μ: NMR: τ 7.79 (singlet, $CCH_3$), 6.54 (singlet, $NCH_3$), and 2.2–3.2 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 1.56 (theoretical, 1.50); UV 243 mμ (ε 9890), 284 mμ (ε 11,900), and 333 mμ (ε 4620).

(*XIII*). IR: 11.35 and 12.28 μ (1,2,4-trisubstitution); far IR: 15.40, 17.04, 19.09, 21.08, and 22.56 μ; NMR: τ 6.52 (singlet, $NCH_3$) and 2.5–3.1 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 2.07 (theoretical, 2.0); UV: 243 mμ (ε 22,500), 290 mμ (ε 31,800), and 335 mμ (ε 11,200).

*5-Methyl-10-phenyl-5,10-dihydrophenophosphazine.* A mixture of (IV) (1.0 g, 0.003 mole) and phenyldichlorophosphine (0.54 g, 0.003 mole) was heated at 180° for 2 h. The temperature was raised to 210°, and the mixture was vacuum-distilled (3 mm) to give dimethyltin dichloride, m.p. 105–107°, no depression on admixture with an authentic sample.

The residue was stirred with 25 ml of hot benzene, and the mixture was filtered. Removal of the benzene from the filtrate left a solid which was recrystallized from ethanol to give 0.52 g (59%) of product, m.p. 158–160° (lit.[8] 159–160°), no depression on admixture with an authentic sample, infrared spectrum superimposable on that of an authentic sample; IR: 13.35 and 14.38 μ (1,2-disubstitution, monosubstitution); far IR: 15.00, 16.49, 17.29, 18.14, 18.79, 19.79, 20.88, 21.78, 22.78, 24.03, 25.57, and 28.07 μ; NMR: τ 6.75 (singlet, $NCH_3$) and 2.1–3.4 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 4.42 (theoretical, 4.34); UV: 245 mμ (ε 16,200), 280 mμ (ε 14,000), 308 mμ (ε 7520), and 340 mμ (ε 6940).

*2,5,8-Trimethyl-10-phenyl-5,10-dihydrophenophosphazine.* A mixture of (VI) (1.0 g, 0.0028 mole) and phenyldichlorophosphine (0.5 g, 0.0028 mole) was heated at 160° for 2 h. The temperature was raised to 195°, and the mixture was vacuum-distilled (2.5 mm) to give dimethyltin dichloride, m.p. 104–106°. The residue was stirred with 25 ml of hot benzene, and the mixture was filtered. The residue was recrystallized from ethanol to give 0.32 g (36%) of product, m.p. 144–146°, no depression on admixture with a sample obtained by allowing N-methyl-2,2'-dilithiodi-*p*-tolylamine[11] to react with phenyldichlorophosphine. (Found: C, 79.42; H, 6.33; N, 4.59; mol.wt. in 2-butanone, 316. $C_{21}H_{20}NP$ calcd.: C, 79.47; H, 6.35; N, 4.41%; mol.wt., 317.37.) IR: 11.10, 12.28, and 12.42 μ (1,2,4-trisubstitution) and 14.32 μ (monosubstitution); far IR: 16.19, 17.24, 17.79, 18.24, 18.59, 19.74, 20.98, 22.38, 23.38, 25.32, 26.32, and 28.07 μ; NMR: τ 7.70 (singlet, $CCH_3$), 6.82 (singlet, $NCH_3$), and 2.4–3.3 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 1.12 (theoretical, 1.22); UV: 245 mμ (ε 18,200), 281 mμ (ε 15,900), 320 mμ (ε 6880), and 348 mμ (ε 7090).

*2,8-Dibromo-5-methyl-10-phenyl-5,10-dihydrophenophosphazine.* A mixture of (VIII) (10.0 g, 0.021 mole) and phenyldichlorophosphine (3.67 g, 0.021 mole) was heated at 210° for 2 h and then vacuum distilled (1.5 mm) at 210° to give 2.75 g (61%) of dimethyltin dichloride, m.p. 104–106°. The residue was stirred with 50 ml of hot benzene, and the mixture was filtered. Removal of the benzene from the filtrate left a solid which was recrystallized from ethyl acetate to give 5.0 g (55%) of product, m.p. 227–229°, no depression on admixture with a sample obtained by allowing N-methyl-2,2'-dilithio-4,4'-dibromodiphenylamine[2,12] to react with phenyldichlorophosphine. (Found: C, 51.08; H, 3.25; N, 3.17; Br, 35.65; mol.wt. in 2-butanone, 466.

$C_{19}H_{14}Br_2NP$ calcd.: C, 51.04; H, 3.16; N, 3.13; Br, 35.75%; mol.wt., 447.14.) IR: 11.20 and 12.32 $\mu$ (1,2,4-trisubstitution) and 14.40 $\mu$ (monosubstitution); far IR: 15.44, 16.54, 17.99, 18.84, 19.94, 21.08, 21.68, 22.78, 24.73, and 27.02 $\mu$; NMR: $\tau$ 6.63 (singlet, $NCH_3$) and 2.1–3.2 (multiplet, aromatic CH); ratio of aromatic/aliphatic protons, 4.14 (theoretical, 3.66); UV: 245 m$\mu$ ($\varepsilon$ 28,700), 291 m$\mu$ ($\varepsilon$ 35,000), 318 m$\mu$ ($\varepsilon$ 16,800), 335 m$\mu$ ($\varepsilon$ 11,200), and 345 m$\mu$ ($\varepsilon$ 10,400).

*Acknowledgement*

The authors wish to thank Professor HAROLD A. HORAN for the infrared and ultraviolet spectral data.

*Department of Chemistry,*
*St. John's University,*
*Jamaica, New York 11432 (U.S.A.)*

EUGENE J. KUPCHIK
VINCENT A PERCIACCANTE

1 H. GILMAN AND E. A. ZUECH, *J. Am. Chem. Soc.*, 82 (1960) 2522.
2 D. WASSERMAN, R. E. JONES, S. A. ROBINSON AND J. D. GARBER, *J. Org. Chem.*, 30 (1965) 3248.
3 K. A. KOCHESHKOV, *Ber.*, 62 (1929) 996; 66 (1933) 1661.
4 H. G. KUIVILA AND O. F. BEUMEL, JR., *J. Am. Chem. Soc.*, 80 (1958) 3250.
5 C. M. SILCOX AND J. J. ZUCKERMAN, *J. Am. Chem. Soc.*, 88 (1966) 168.
6 C. H. YODER AND J. J. ZUCKERMAN, *J. Am. Chem. Soc.*, 88 (1966) 2170.
7 D. SEYFERTH, *Naturwissenschaften*, 44 (1957) 34.
8 G. BAUM, H. A. LLOYD AND C. TAMBORSKI, *J. Org. Chem.*, 29 (1964) 3410.
9 C. TOMLINSON, *Mikrochim. Acta*, 3 (1961) 457.
10 H. GILMAN AND E. A. ZUECH, *J. Org. Chem.*, 26 (1961) 2013.
11 H. GILMAN AND E. A. ZUECH, *J. Org. Chem.*, 27 (1962) 2897.
12 C. S. GIBSON AND D. C. VINING, *J. Chem. Soc.*, (1923) 831; K. FRIES, *Ann. Chem.*, 346 (1906) 128; A. E. ERICKSON, R. J. TULL AND W. A. SKLAVZ, Merck and Co., Inc., *Fr.P.*1,322,421, Mar. 29, 1963; U. S. Appl. Mar. 31, 1961.

Received March 13th, 1967