[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

Synthesis of Some 5,10-Dihydrophenazasiline Derivatives

HENRY GILMAN AND ERNEST A. ZUECH

Received September 20, 1960

Several 5,10-dihydrophenazasiline derivatives have been prepared by a cyclization reaction from *N*-substituted 2,2′-dilithiodiarylamine intermediates and diphenyldichlorosilane, dibenzyldichlorosilane or methylphenyldichlorosilane. Also, four 10,10′-spirobi(5,10-dihydrophenazasiline) compounds have been synthesized in a similar fashion from silicon tetrachloride. Two functional 5,10-dihydrophenazasiline derivatives, *i.e.*, having a silicon-hydrogen grouping, have been obtained by treating *N*-ethyl-2,2′-dilithiodiphenylamine with phenylsilane and with *n*-hexadecylsilane. These functional derivatives have been treated with a variety of organolithium reagents to give the corresponding substitution products in good yields.

The first 5,10-dihydrophenazasiline compounds were synthesized in low yields by the extended heating of diphenylsilane with phenothiazine derivatives.[1] Recently, we have reported the successful preparation of 5,10-dihydrophenazasiline compounds by a new method, which involves cyclization reactions of appropriately substituted halosilanes with *N*-ethyl-2,2′-dilithiodiarylamine.[2] Thus, 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline and 5,5′-diethyl-10,10′-spirobi(5,10-dihydrophenazasilane) were obtained by treating diphenyldichlorosilane and silicon tetrachloride with one and two molar equivalents, respectively, of *N*-ethyl-2,2′-dilithiodiphenylamine. In these studies, this new method of synthesis has been more thoroughly investigated and broadened to include both functional and many nonfunctional types.

The products of the cyclization reactions of *N*-substituted 2,2′-dilithiodiarylamine intermediates with dichloroörganosilanes are summarized in Table I. Thus, by varying either one or both of the reactants a wide variety of compounds has been prepared. Treatment of methylphenyldichlorosilane and dibenzyldichlorosilane with *N*-ethyl-2,2′-dilithiodiphenylamine[2] gave 5-ethyl-10-methyl-10-phenyl-5,10-dihydrophenazasiline (I) and 5-ethyl-10,10-dibenzyl-5,10-dihydrophenazasiline (II).

The synthesis of some 5-methyl and 5-phenyl derivatives of 5,10-dihydrophenazasiline has been accomplished by starting with the corresponding *N*-methyl and *N*-phenyl compounds of 2,2′-dibromodiphenylamine. *N*-Methyl-2,2′-dibromodiphenylamine was prepared by reacting 2,2′-dibromodiphenylamine[3] with methyllithium and then with a refluxing tetrahydrofuran solution of dimethyl sulfate. Reaction of this compound with *n*-butyllithium and subsequent treatment with diphenyldichlorosilane gave the known compound, 5 - methyl - 10,10 - diphenyl-5,10-dihydrophenazasiline (III).[1] The 10,10-dibenzyl derivative IV was prepared in like manner.

The *N*-phenyl compound, 2,2′-dibromotriphenylamine, was obtained by heating a mixture of 2,2′-dibromodiphenylamine, iodobenzene, anhydrous potassium carbonate, and copper-bronze. The dilithium compound was then formed by halogen-metal interconversion and treated with diphenyldichlorosilane to give 5,10,10-triphenyl-5,10-dihydrophenazasiline (V).

In order to obtain the 2-substituted compounds VI and VII, it was first necessary to synthesize the appropriately substituted amine intermediates. Here, the very versatile Chapman rearrangement[4] was utilized. 2-Bromophenylbenzimidoyl chloride was prepared according to the procedure of Jones and Mann,[3] and allowed to react with the sodium salts of 2-bromo-4-chlorophenol and of 2-bromo-4-phenylphenol. The resulting benzimidoate esters were thermally rearranged and subsequently hydrolyzed to give 2,2′-dibromo-4-chlorodiphenylamine and 2,2′-dibromo-4-phenyldiphenylamine, respectively. Procedures, used to prepare the *N*-ethyl[2] and *N*-methyl derivatives of 2,2′-dibromodiphenylamine, were employed to convert these amines to the corresponding *N*-ethyl compounds. The 2-substituted 5,10-dihydrophenazasiline compounds VI and VII were ultimately obtained by treating the *N*-ethyl compounds with *n*-butyllithium and then with diphenyldichlorosilane.

The 10,10′-spirobi(5,10-dihydrophenazasiline) compounds listed in Table II were prepared by techniques similar to those used for the compounds in Table I. 5,5′-Dimethyl-10,10′-spirobi(5,10-dihydrophenazasiline) (VIII), for example, was obtained by treating silicon tetrachloride with two molar equivalents of *N*-methyl-2,2′-dilithiodiphenylamine.

The synthesis of unsymmetrical 5,10-dihydrophenazasiline compounds containing different organic groups attached to silicon is complicated by the inaccessibility of unsymmetrical diorganosilicon halides. Therefore, it was of interest to prepare phenazasiline types having a functional group

---

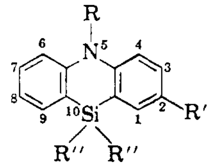
[1] H. Gilman and D. Wittenberg, *J. Am. Chem. Soc.*, **79**, 6339 (1957); D. Wittenberg, H. A. McNinch, and H. Gilman, *J. Am. Chem. Soc.*, **80**, 5418 (1958).

[2] H. Gilman and E. A. Zuech, *Chem. & Ind.*, 1227 (1958); *J. Am. Chem. Soc.*, **82**, 2522 (1960).

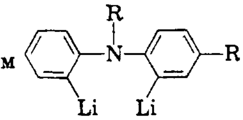
[3] E. R. H. Jones and F. G. Mann, *J. Chem. Soc.*, 786 (1956).

[4] A. W. Chapman, *J. Chem. Soc.*, 1743 (1927); 569 (1929).

TABLE I



COMPOUNDS FROM

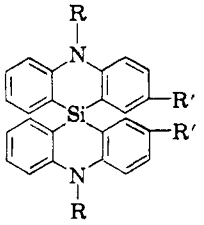


AND R''_2SiCl_2[a] IN REFLUXING DIETHYL ETHER

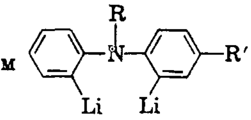
No.	R	R′	R″	Time, (hr.)	Yield, %	M.P.	Solvent[b] for Crystal.	Empirical Formula	Silicon, % Calcd.	Silicon, % Found
I	C_2H_5—	H—	C_6H_5—(CH_3—)[a]	17[c]	72	62–64	A	$C_{21}H_{21}NSi$	8.90	8.92, 8.80
II	C_2H_5—	H—	$C_6H_5CH_2$—	16[d]	58	71–73[e]	A	$C_{28}H_{27}NSi$	6.93	6.81, 6.83
III	CH_3—	H—	C_6H_5—	17	64	182–184	B	$C_{25}H_{21}NSi$	—	— —
IV	CH_3—	H—	$C_6H_5CH_2$—	16[d]	36	126–127.5	B	$C_{27}H_{25}NSi$	7.17	7.23, 7.18
V	C_6H_5—	H—	C_6H_5—	24[c]	32	210–212	B	$C_{30}H_{23}NSi$	6.60	6.29, 6.42[f]
VI	C_2H_5—	Cl—	C_6H_5—	5[g]	27	121–122	B	$C_{26}H_{22}ClNSi$	6.82	6.83, 6.70[h]
VII	C_2H_5—	C_6H_5—	C_6H_5—	4[i]	34	145.5–147	B	$C_{32}H_{27}NSi$	6.19	6.25, 6.22[j]

[a] Compound I was prepared from methylphenyldichlorosilane. [b] A, absolute ethanol; B, petroleum ether (b.p. 60–70)°. [c] Color Test I remained positive. Toluene was added, the ether removed by distillation, and the toluene suspension refluxed for 2 hr. before the color test was negative. [d] Toluene suspension refluxed 3 hr. [e] B.p. 204–212 (0.005 mm.). [f] Calcd.: C, 84.66; H, 5.45; N, 3.29. Found: C, 85.13; H, 5.52; N, 3.19. [g] Toluene suspension refluxed 18 hr. [h] *Anal.* Calcd.: C, 75.79; H, 5.38; Cl, 8.61. Found: C, 76.22, 76.04; H, 5.26, 5.41; Cl, 8. 47, 8.66. [i] Toluene suspension refluxed 19 hr. [j] *Anal.* Calcd.: N, 3.09. Found: N, 3.20, 2.98.

TABLE II



COMPOUNDS FROM



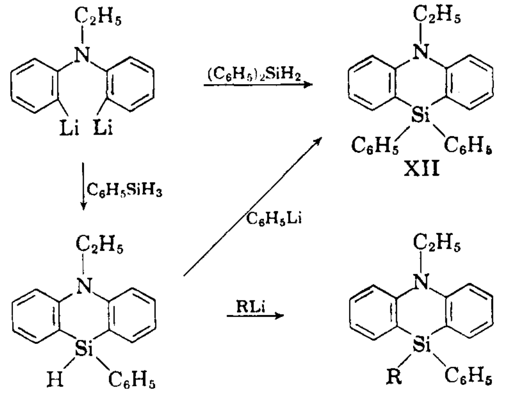
AND $SiCl_4$ IN REFLUXING DIETHYL ETHER

No.	R	R′	Time, (hr.)	Yield, %	M.P.	Solvent[a] for Crystal.	Empirical Formula	Silicon, % Calcd.	Silicon, % Found
VIII	CH_3—	H—	18[b]	57	247–249	C	$C_{26}H_{22}N_2Si$	7.19	7.08, 7.19
IX	C_6H_5—	H—	18	24	313–314	C	$C_{36}H_{26}N_2Si$	5.46	5.40, 5.37
X	C_2H_5—	Cl—	24[c]	30	189–191	D	$C_{28}H_{24}Cl_2N_2Si$	5.76	5.87, 5.80[d]
XI	C_2H_5—	C_6H_5—	24[c]	41	235–238	D	$C_{40}H_{34}N_2Si$	4.92	4.97, 5.04[e]

[a] C, ethyl acetate; D, petroleum ether (b.p. 60–70°)-benzene (1:1). [b] Color Test I remained positive. Toluene was added, the ether removed by distillation, and the toluene suspension refluxed for 1.5 hr. before the color test was negative. [c] Toluene suspension refluxed 1 hr. [d] Calcd.: C, 68.98; H, 4.96. Found: C, 69.04, 69.22; H, 4.79, 4.60. [e] *Anal.* Calcd.: C, 84.16; H, 6.00. Found: C, 84.82, 84.62; H, 5.75, 5.96.

which could subsequently be allowed to react with various organolithium reagents. This approach has previously been exploited quite successfully in the synthesis of unsymmetrical dibenzosilole derivatives.[5]

The difficulties encountered in the handling and storing of silicon halides prompted the investigation of organosilicon hydrides[6] in this cyclization reaction with the aim of preparing silicon-hydride functional compounds. In an orienting experiment to determine the course of the reaction, *N*-ethyl-2,2′-dilithiodiphenylamine was treated with diphenylsilane. 5-Ethyl - 10,10 - diphenyl - 5,10 - dihydrophenazasiline (XII) was produced in a 36% yield. Accordingly, phenylsilane was treated with the dilithium compound to give the silicon-hydride functional compound, 5-ethyl-10-phenyl-5,10-dihydrophenazasiline, in an 80% yield. This compound,

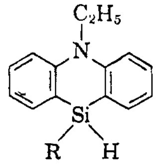


---

(5) H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **80**, 1883 (1958).

(6) For reactions of organosilicon hydrides with organometallic compounds, see H. Gilman and E. A. Zuech, *J. Am. Chem. Soc.*, **81**, 5925 (1959).

TABLE III

5-ETHYL-5,10-DIHYDROPHENAZASILINE COMPOUNDS FROM THE REACTION OF  WITH R'Li IN REFLUXING DIETHYL ETHER

No.	R	R'Li R'	Time, (hr.)	Yield, %	M.P.	Solvent[a] for Crystal.	Empirical Formula	Silicon, % Calcd.	Silicon, % Found
XII	C_6H_5—	C_6H_5—	17	69	121–122	B	$C_{26}H_{23}NSi$	—	— —
XIII	C_6H_5—	4-$CH_3C_6H_4$—	5	70	102–103.5	E	$C_{27}H_{25}NSi$	7.17	7.08, 7.06
XIV	C_6H_5—	2-$C_6H_5C_6H_4$—[b]	16	73	121.5–124	F	$C_{32}H_{27}NSi$	6.19	6.28, 6.15
XV	C_6H_5—	4-$C_6H_5OC_6H_4$—[c]	16	59	98.5–100	G	$C_{32}H_{27}NOSi$	5.98	6.17, 5.88
XVI	C_6H_5—	4-BrC_6H_4—[c]	18[d]	39	159–160.5	D	$C_{26}H_{22}BrNSi$	6.15	6.32, 6.18
XVII	C_6H_5—	4,4'-$C_6H_4C_6H_4$—[c,e]	18[f]	49	246–248	G	$C_{52}H_{44}N_2Si_2$	7.48	7.24, 7.29
XVIII	n-$C_{16}H_{33}$—	C_6H_5—	18	50	227–230[g] (0.004)	—	$C_{36}H_{51}NSi$	5.34	5.36, 5.36
XIX	n-$C_{16}H_{33}$—	4-$CH_3C_6H_4$—	18	47	220–225[g] (0.003)	—	$C_{37}H_{53}NSi$	5.20	5.09, 5.22[h]

[a] B, petroleum ether (b.p. 60–70°); D, petroleum ether–benzene (1:1); E, petroleum ether–absolute ethanol (1:1); F, 95% ethanol; G, benzene-absolute ethanol (1:1). [b] H. Gilman and K. Oita, *J. Org. Chem.*, **20**, 862 (1955). [c] H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1940). [d] Room temperature. [e] *p*-Biphenylenedilithium. [f] Refluxing benzene. [g] B.p., °C. (mm.). [h] *Anal.* Calcd.: C, 82.31; H, 9.89. Found: C, 82.84, 83.02; H, 9.92, 9.72.

upon reaction with an ethereal solution of phenyllithium, gave the known derivative XII, thereby substantiating the proposed structure. In similar fashion, the compound reacted with various organolithium reagents to give the unsymmetrically substituted derivatives in good to excellent yields. (Table III).

Another functional phenazasiline type, 5-ethyl-10-*n*-hexadecyl-5,10-dihydrophenazasiline, was prepared by treating *N*-ethyl-2,2'-dilithiodiphenylamine with *n*-hexadecylsilane. Treatment of this substance with organolithium reagents afforded the unsymmetrical derivatives, as described above (Table III).

EXPERIMENTAL[7]

A detailed description of the steps leading to 5-methyl-10,10-dibenzyl-5,10-dihydrophenazasiline (IV) is illustrative of the method used in the preparation of the compounds listed in Tables I and II. Significant variations in the procedures and other data of value are collected in the tables.

5-Methyl-10,10-dibenzyl-5,10-dihydrophenazasiline (IV). *N*-Methyl-2,2'-dibromodiphenylamine (6.82 g., 0.02 mole) in 100 ml. of ether, cooled in an ice bath, was treated with 0.04 mole of an ethereal solution of *n*-butyllithium. Color Test II[8] was negative after stirring for 1 hr. A solution of 5.60 g. (0.02 mole) of dibenzyldichlorosilane in 25 ml. of ether was added, and the reaction mixture heated at reflux for 16 hr. Since Color Test I[9] remained positive, 50 ml. of toluene was added and the ether removed by distillation. After refluxing the toluene suspension for 3 hr., the color test was negative and the reaction mixture was poured upon crushed ice. The aqueous layer was separated, extracted with ether, and discarded. The combined organic solutions were dried with anhydrous sodium sulfate and evaporated. Treatment of the oily residue with petroleum ether (b.p. 60–70°) gave 3.67 g. of a tan solid, m.p. 113–125°. This material was recrystallized twice from petroleum ether to give 2.78 g. (36%) of colorless needles, m.p. 126–127.5°. An additional recrystallization did not change the melting point (see Table I).

N-Methyl-2,2'-dibromodiphenylamine. Methyllithium (0.11 mole) was added to 30 g. (0.092 mole) of 2,2'-dibromodiphenylamine[3] in 100 ml. of ether and cooled in an ice bath. After stirring for 1 hr., a solution of 15 g. (0.12 mole) of freshly distilled dimethyl sulfate in 100 ml. of tetrahydrofuran was added, and the ether removed by distillation. The resulting solution was heated at reflux for 18 hr. and, after cooling, hydrolyzed with iced water. The aqueous layer was separated, extracted with ether, and discarded. After drying the combined organic solutions with anhydrous sodium sulfate, the solvent was removed by distillation. The residue was taken up in petroleum ether (b.p. 60–70°) to give 27.8 g. (89%) of colorless crystals, m.p. 106–109°. The analytical sample melted at 106–107°.

Anal. Calcd. for $C_{13}H_{11}Br_2N$: N, 4.11. Found: N, 4.17, 4.10.

2,2'-Dibromotriphenylamine. A mixture of 10.3 g. (0.0314 mole) of 2,2'-dibromodiphenylamine,[3] 18.3 g. (0.09 mole) of iodobenzene, 8 g. of anhydrous potassium carbonate, and 0.5 g. of copper-bronze was heated from 175 to 200° for 24 hr. The reaction mixture was allowed to cool, treated with 200 ml. of ether, and filtered. The ether was evaporated and the resulting material dissolved in absolute ethanol. After standing for 5 days, a light brown solid was deposited. This was taken up in hot 95% ethanol, treated with charcoal, and cooled to give 5.37 g. (43%) of colorless crystals, m.p. 106–109°. Recrystallization from the same solvent raised the melting point to 108.5–110°.

Anal. Calcd. for $C_{18}H_{13}Br_2N$: N, 3.47. Found: N, 3.47, 3.52.

A similar reaction employing 22.9 g. of 2,2'-dibromodiphenylamine gave only a 28% yield of 2,2'-dibromotriphenylamine.

2-Bromo-4-chlorophenyl N-2-bromophenylbenzimidoate. Sodium ethoxide was prepared by treating 10.3 g. (0.45 g.-atom) of sodium with 300 ml. of absolute ethanol. After cooling the solution in an ice bath, 95 g. (0.46 mole) of 2-bromo-4-chlorophenol in 100 ml. of ether was added, fol-

---

(7) All melting and boiling points are uncorrected, and all reactions involving organometallic reagents were carried out under an atmosphere of dry, oxygen-free nitrogen in sodium dried solvents.

(8) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

(9) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

lowed by a solution of 133 g. (0.45 mole) of 2-bromophenylbenzimidoyl chloride[3] in 100 ml. of ether. The reaction mixture was stirred at room temperature for 16 hr., and then concentrated by the distillation of the greater portion of the ethanol. After cooling, hydrolysis was effected by pouring upon crushed ice, and the aqueous layer decanted from the resulting heavy oil. The oil slowly solidified and was recrystallized twice from 95% ethanol to give 148 g. (71%) of colorless crystals, m.p. 70–72°. The analytical sample melted at 71–72°.

Anal. Calcd. for $C_{19}H_{12}Br_2ClNO$: C, 49.01; H, 2.60; N, 3.01. Found: C, 49.32, 49.19; H, 2.69, 2.65; N, 3.21, 3.19.

N-Benzoyl-2,2′-dibromo-4-chlorodiphenylamine. 2-Bromo-4-chlorophenyl *N*-2-bromophenylbenzimidoate (15 g., 0.032 mole) was heated from 230 to 240° for 2.5 hr. The resulting black material was dissolved in 50 ml. of absolute ethanol, treated with charcoal twice, and concentrated depositing 6.25 g. (42%) of tan crystals, m.p. 120–125°. Two additional recrystallizations from the same solvent raised the melting point to 127–128.5°.

Anal. Calcd. for $C_{19}H_{12}Br_2ClNO$: C, 49.01; H, 2.60; N, 3.01. Found: C, 49.09; H, 2.83; N, 2.99.

The yields from two similar runs were 52 and 55%, respectively.

2,2′-Dibromo-4-chlorodiphenylamine. A mixture of 18.5 g. (0.04 mole) of *N*-benzoyl-2,2′-dibromo-4-chlorodiphenylamine, 20 g. of potassium hydroxide, 20 ml. of water, and 150 ml. of 95% ethanol was heated at reflux for 18 hr. The reaction mixture was concentrated by distilling approximately 150 ml. of solvent and then poured upon crushed ice. After extracting the aqueous solution with ether, the organic solution was dried with anhydrous sodium sulfate and distilled. The residue was taken up in absolute ethanol, treated with charcoal, and reduced in volume to give 11.25 g. (79%) of colorless solid, m.p. 81–83°. Recrystallization from the same solvent gave white flakes, m.p. 81–82.5°.

Anal. Calcd. for $C_{12}H_8Br_2ClN$: C, 39.87; H, 2.23; N, 3.88. Found: C, 39.88; H, 2.33; N, 4.00.

In two similar runs, 2,2′-dibromo-4-chlorodiphenylamine was prepared in yields of 71% and 73%.

N-Ethyl-2,2′-dibromo-4-chlorodiphenylamine. A solution of 21 g. (0.058 mole) of 2,2′-dibromo-4-chlorodiphenylamine in 100 ml. of ether was treated with 0.06 mole of an ethereal solution of methyllithium, while cooling in an ice bath. After stirring for 1 hr., 9.24 g. (0.06 mole) of freshly distilled diethyl sulfate in 70 ml. of tetrahydrofuran was added and the ether was removed by distillation. The resulting solution was refluxed for 16 hr. and then hydrolyzed with 100 ml. of water. The reaction products were worked up in the usual manner and distilled at reduced pressure to give 17.7 g. (78%) of pale yellow viscous oil, b.p. 142–146° (0.005 mm.), n_D^{20} 1.6437. Attempts to crystallize the material were unsuccessful.

Anal. Calcd. for $C_{14}H_{12}Br_2ClN$: N, 3.60. Found: N, 3.68, 3.64.

In an analogous run, the ethylated compound was obtained in an 81% yield.

3-Bromobiphenyl-4-yl N-2-bromophenylbenzimidoate. A solution of 130 g. (0.56 mole) of 2-bromo-4-phenylphenol in 300 ml. of ether was added to 0.55 mole of sodium ethoxide in 700 ml. of absolute ethanol, while cooling in an ice bath. This solution was then treated with 161 g. (0.55 mole) of 2-bromophenylbenzimidoyl chloride[3] in 100 ml. of ether. After stirring for 16 hr., the solution was concentrated by distillation, cooled, and poured upon crushed ice. The aqueous solution was decanted from the resulting sticky solid, which was recrystallized from ethyl acetate to give 208 g. (74%) of colorless crystals, m.p. 146–149°. Two recrystallizations of a portion from ethyl acetate raised the melting point to 149–151°.

Anal. Calcd. for $C_{25}H_{17}Br_2NO$: C, 59.19; H, 3.38; N, 2.76. Found: C, 59.76, 59.83; H, 3.40, 3.52; N, 2.56, 2.67.

N-Benzoyl-2,2′-dibromo-4-phenyldiphenylamine. 3-Bromobiphenyl-4-yl *N*-2-bromophenylbenzimidoate (25 g., 0.049 mole) was heated from 240 to 255° for 2.5 hr. The black reaction mixture was then digested with 50 ml. of ethyl acetate. After cooling, the solution was filtered, reduced in volume (*ca.* 20 ml.), and filtered again. A total of 19.9 g. (80%) of tan solid, m.p. 204–208°, was collected. A portion was recrystallized twice from ethyl acetate and then from benzene to give colorless crystals, m.p. 209–211°.

Anal. Calcd. for $C_{25}H_{17}Br_2NO$: N, 2.76. Found: N, 2.73, 2.71.

In two similar runs, the yields of rearrangement product were 68 and 69%, respectively.

2,2′-Dibromo-4-phenyldiphenylamine. A mixture of 27 g. (0.053 mole) of *N*-benzoyl-2,2′-dibromo-4-phenyldiphenylamine, 100 g. of potassium hydroxide, and 700 ml. of 95% ethanol was refluxed for 19 hr. The solution was concentrated by distillation and then poured upon crushed ice. The aqueous solution was extracted with ether and discarded. After drying and distilling the organic layer, the residue was taken up in absolute ethanol, treated with charcoal, and reduced in volume to give 16.7 g. (78%) of pale yellow crystals, m.p. 82.0–83.5°. Recrystallization from the same solvent gave lustrous crystals, m.p. 82–83°.

Anal. Calcd. for $C_{18}H_{13}Br_2N$: C, 53.61; H, 3.25; N, 3.48. Found: C, 54.01, 53.98; H, 3.39, 3.35; N, 3.40, 3.44.

N-Ethyl-2,2′-dibromo-4-phenyldiphenylamine. A solution of 19.9 g. (0.049 mole) of 2,2′-dibromo-4-phenyldiphenylamine in 100 ml. of ether, cooled in an ice bath, was treated with 0.05 mole of an etheral solution of methyllithium After stirring for 1 hr., 8.5 g. (0.055 mole) of freshly distilled diethyl sulfate in 70 ml. of tetrahydrofuran was added. The ether was removed by distillation and the tetrahydrofuran solution heated at reflux for 16 hr. Hydrolysis was effected with water and the reaction mixture worked up in the usual manner. The remaining material was treated with a small amount of absolute ethanol and filtered to give 17.6 g. of brown solid, m.p. 90–95°. This material was recrystallized from absolute ethanol to give 15.7 g. (74%) of colorless crystals, m.p. 92–95°. The analytical sample melted at 93–95°.

Anal. Calcd. for $C_{20}H_{17}Br_2N$: C, 55.71; H, 3.98; N, 3.25. Found: C, 55.88, 55.95; H, 4.09, 3.96; N, 3.46, 3.36.

In a repeat run, the *N*-ethyl derivative was obtained in a 72% yield.

5-Ethyl-10,10-diphenyl-5,10-dihydrophenazasiline from diphenylsilane. A solution of 3.55 g. (0.01 mole) of *N*-ethyl-2,2′-dibromodiphenylamine[2] in 50 ml. of ether, cooled in an ice bath, was treated with 0.02 mole of an ethereal solution of *n*-butyllithium. After stirring for 1 hr., 1.84 g. (0.01 mole) of diphenylsilane[10] dissolved in 50 ml. of dry toluene was added and the reaction mixture heated at reflux for 22 hr. Color Test I[9] was negative and hydrolysis was effected by pouring upon a solution of dilute sulfuric acid. The organic layer was worked up in the usual manner and evaporated under an air-jet. The remaining material was taken up in petroleum ether (b.p. 60–70°) to give 1.64 g. of pale yellow crystals, m.p. 109–120°. This material was then dissolved in hot petroleum ether, decolorized with charcoal, and cooled to give 1.36 g. (36%) of colorless crystals, m.p. 121–123°, which was identified as 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline by mixed melting point and by comparison of the infrared spectra.[1,2]

5-Ethyl-10-phenyl-5,10-dihydrophenazasiline. An ethereal solution containing 0.04 mole of *N*-ethyl-2,2′-dilithiodiphenylamine,[2] prepared as described above, was added over a period of 1 hr. to 5.4 g. (0.05 mole) of phenylsilane[11] in 100 ml. of ether, while cooling in an ice bath. After stirring for 2 hr. at room temperature, Color Test I[9] was negative and hydrolysis was effected by pouring upon crushed ice containing a small amount of sulfuric acid. The organic layer

---

[10] R. A. Benkeser, H. Landesman, and D. J. Foster, *J. Am. Chem. Soc.*, **74**, 648 (1952).

[11] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach, and H. L. Schlesinger, *J. Am. Chem. Soc.*, 69, 2692 (1947).

was separated and dried with anhydrous calcium sulfate, and the ether removed by distillation. The resulting material was distilled at reduced pressure to give 9.6 g. (80%) of a pale yellow viscous oil, b.p. 180–184° (0.014 mm.). This material solidified upon standing to a colorless sticky solid which was extremely difficult to crystallize to a sharp melting point. It was recrystallized finally from petroleum ether (b.p 60–70°) to give colorless needles, m.p. 75–78°.

Anal. Calcd. for $C_{20}H_{19}NSi$: Si, 9.33. Found: Si, 9.08, 9.16.

In another run employing 0.085 mole of *N*-ethyl-2,2′-dilithiodiphenylamine, there was obtained a 78% yield of 5-ethyl-10-phenyl-5,10-dihydrophenazasiline.

5-Ethyl-10-n-hexadecyl-5,10-dihydrophenazasiline. An ethereal solution containing 0.05 mole of *N*-ethyl-2,2′ dilithiodiphenylamine[2] was added over a period of 1.5 hr. to 14.0 g. (0.055 mole) of *n*-hexadecylsilane[12] in 100 ml. of ether, while cooling the reaction flask in an ice-bath. The reaction mixture was warmed to room temperature and refluxed for 2 hr. before Color Test I[9] was negative. After hydrolyzing by pouring upon crushed ice, ether was added, and the organic layer was separated and dried with anhydrous calcium sulfate. The ether was removed by distillation and the resulting oil was distilled at reduced pressure to give 16 g. of turbid liquid, b.p. 193–233° (0.008 mm.). This liquid was then redistilled to give 11.9 g. (53%) of liquid, b.p. 230–235° (0.003 mm.), which solidified upon standing. A portion of this material was recrystallized twice from a 10:1 mixture of methanol and benzene to give colorless crystals, m.p. 51–53°.

Anal. Calcd. for $C_{30}H_{47}NSi$: Si, 6.25. Found: Si, 6.41, 6.29.

Infrared absorption spectra. All of the infrared spectra of the 5,10-dihydrophenazasiline compounds showed a split band of weak to medium intensity in the 9.3 to 9.4 μ region. An absorption band at 13.1–13.2 μ (*o*-disubstitution) was present in all of the spectra, while those of the compounds containing substituents in the 2-position exhibited an additional band at 12.3–12.4 μ (1,2,4-trisubstitution). The two Si-H functional compounds had a strong band at 4.7 μ characteristic of the Si-H grouping.

Acknowedgment. This research was supported in part by the United States Air Force under Contract AF 33(616)-6127 monitored by the Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio. Infrared analyses were obtained through the courtesy of the Institute for Atomic Research, Iowa State University, with special acknowledgment to Dr. V. A. Fassel, Mr. Richard Kniseley, and Miss Evelyn Conrad for the spectra.

AMES, IOWA

---

[12] M. B. Hughes, Ph.D. dissertation, Iowa State University (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

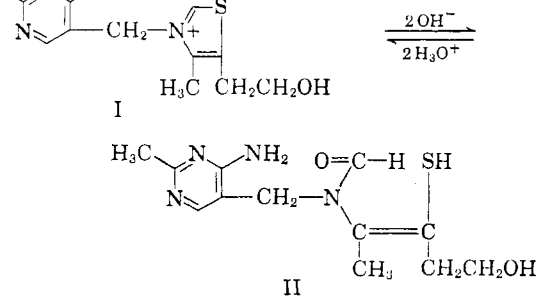
Isomeric S-Methylthiamins[1,2]

EUGENE P. DIBELLA AND DOUGLAS J. HENNESSY

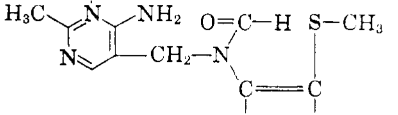
Received June 27, 1960

Two interconvertible isomeric forms of *S*-methylthiamin have been found to exist. The higher melting, more stable form is designated as 2-(4′-amino-2′-methyl-5′-pyrimidylmethylformamido)-2-methyl-3-methylmercaptotetrahydrofuran. The lower melting, less stable form is designated as 4-(4′-amino-2′-methyl-5′-pyrimidylmethylformamido)-3-methylmercapto-4-methyl-Δ³-pentenol.

The hypothesis put forth in 1940 by Zima and Williams[3] suggests that thiamin (I) exercises some of its vital physiological functions in the so-called open form (II). The latter arises *in vitro* from I by the action of two equivalents of alkali.[4]



We planned the preparation of a structurally simple, locked open form of thiamin which might prove useful in testing this and other hypotheses on the functioning of thiamin. The preparation of *S*-methylthiamin (III) was attempted by reaction of I with three equivalents of aqueous alkali and one of dimethyl sulfate or methyl iodide. A product was obtained whose elementary analysis corresponded to the desired compound. It melted at 193°.


III

Shortly afterwards, however, Sykes and Todd[5] reported the preparation of an *S*-methylthiamin of melting point 133° by a procedure which utilized

---

[1] This work formed part of the Ph.D. thesis of Eugene P. DiBella, Fordham University, 1953, and was supported by a grant-in-aid from the Williams-Waterman Fund of the Research Corporation.

[2] Presented before the 122nd Meeting of the American Chemical Society at Atlantic City, September 1952.

[3] O. Zima and R. R. Williams, *Ber.*, **73**, 941 (1940).

[4] R. R. Williams and A. E. Ruehle, *J. Am. Chem. Soc.*, **57**, 1856 (1935).

[5] P. Sykes and A. R. Todd, *J. Chem. Soc.*, 534 (1951).