Experimental[12,13]

Reaction of Benzyne with Phenyl Isocyanate in Benzene.—The combined product resulting from the diazotization of two portions of 2.74 g. (0.04 *M* total) of anthranilic acid according to the procedure of Stiles, Miller, and Burckhardt[6] was added to 25 ml. of benzene and 10 ml. (~0.08 *M*) of phenyl isocyanate. The resulting mixture was stirred mechanically and heated under gentle reflux for 12 hr. The solvent and excess phenyl isocyanate were removed by lyophilization. The residue in approximately 5 ml. of benzene was introduced onto a column (50 cm.) containing 85 g. of Florisil prepared with hexane. Hexane, benzene, ethyl acetate, and methanol were used as elution solvents. The products were eluted from the column in the order mentioned; yields reported are of isolated crystalline material: (A) phenyl isocyanate dimer, 0.029 g., m.p. 168–172° (lit.[10] m.p. 176°); (B) 9-phenoxyphenanthridine (4), 0.424 g., m.p. 110–119° (Recrystallization from ethanol gave needles, m.p. 118–119°. Positive identification was made by comparison of an infrared spectrum with that of an authentic sample.[14] A mixture melting point was undepressed.); (C) 1,3,5-triphenylbiuret, 0.337 g., m.p. 150–151° (lit.[11] m.p. 150–151°); (D) phenanthridinone, 0.110 g., m.p. 285–290° with sublimation (An authentic sample[15] exhibited identical infrared spectral and melting point behavior.); (E) A total of 0.249 g. of highly colored, heterogeneous material was eluted with the more polar solvents. This material was not further investigated.

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[12] Melting points were determined with a Kofler hot-stage microscope and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 237 recording spectrophotometer. Mass spectra were recorded with a Consolidated Electrodynamics Corp., Type 21-103C mass spectrophotometer. Microanalytical data were supplied by Dr. S. M. Nagy and his associates.

[13] We are indebted to Mr. Heinrich K. Schnoes for the measurement and interpretation of mass spectra of the products. These data greatly simplified the problem of structure elucidation.

[14] We are indebted to Professor D. H. Hey, King's College, London, for a generous sample of authentic 9-phenoxyphenanthridine.

[15] Purchased from Aldrich Chemical Co.

A New Synthesis of 5,10-Dihydrophenazasilines

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The phenazasilines have been shown to have excellent high-temperature stability coupled with antioxidant activity. Their main use has been in the stabilization of polyester lubricants used in high-speed jet engines. An improved synthesis for these compounds was needed.

Previous work in this field was pioneered by Gilman and co-workers. They prepared 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline by the high-temperature reaction between diphenylsilane and N-ethylphenothiazine.[1,2] Yields of only 6–7% were thus obtained.

A better method for preparing the phenazasilines was reported soon after by Gilman and Zuech.[3] However, the key intermediate, 2,2′-dibromodiphenylamine was obtained by a sophisticated but lengthy synthesis using the Chapman rearrangement.[4]

The new synthesis developed in our laboratory is shown in Scheme I which represents a simpler scheme of obtaining these compounds. The key intermediate was the 2,2′-dilithio derivative of N-ethyl-4,4′-dibromodiphenylamine (III) necessary for cyclization with diphenyldichlorosilane to the phenazasiline (IV). This entailed using N-ethyl-2,2′,4,4′-tetrabromodiphenylamine (II). The reaction of the latter compound (II) with 2 equiv. of *n*-butyllithium at 0° resulted in halogen–metal interconversion of the 2,2′-bromine atoms without appreciable reaction of the 4,4′-bromine atoms, yielding compound III. Reaction with dichlorodiphenylsilane produced the 2,8-dibromo-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (IV) in yields as high as 85%. The latter compound is converted to 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (V) either by direct catalytic hydrogenation with palladium on carbon in the presence of sodium or potassium acetate or by an interconversion reaction with *n*-butyllithium at 25° (IX) followed by water hydrolysis. If the 2,8-dilithio intermediate is treated with methyl iodide, the 2,8-dimethyl-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (X) is produced.

The use of dimethyldichlorosilane instead of diphenyldichlorosilane yielded 2,8-dibromo-5-ethyl-10,-10-dimethyl-5,10-dihydrophenazasiline (XI). Substitution of silicon tetrachloride for diphenyldichlorosilane yielded the 2,2′,8,8′-tetrabromo-5,5′-diethyl-10,10-spirobi(5,10-dihydrophenazasiline) (VI) which was converted to the debrominated compound (VII) by hydrogenation.

Derivatives based on tin may also be used instead of silicon. Thus, using diphenyltin dichloride instead of diphenyldichlorosilane, we obtain the corresponding tin compound VIII.

This new route to phenazasilines, starting with diphenylamine and involving four relatively easy steps, is accomplished in 40–43% over-all yield. Readily obtained intermediates such as the 2,8-dibromo-5-alkyl-10,10-diphenyl-5,10-dihydrophenazasiline (IV) can be converted to substituted alkyl- and aryl-substituted phenazasilines through the 2,8-dilithio derivative IX. The dibromo compound is obtained pure without the side reactions that occur on bromination of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline as shown by Gilman and Zuech.[5]

A comprehensive account of other recent work in the field of organometallics as high-temperature additives for lubricants was given by Tamborski.[6] Preparation of the phosphorus analog of these compounds was recently described by the same laboratory.[7]

Experimental[8]

2,2′,4,4′-Tetrabromo-N-ethyldiphenylamine (II).—A suspension of 2,2′,4,4′-tetrabromodiphenylamine[9] (48.5 g., 0.1 mole) in dry tetrahydrofuran (250 g.) was treated with 0.104 moles of methyllithium in ether[10] at 20–24°. After distillation of the ether a tetrahydrofuran solution of diethyl sulfate (15.4 g., 0.1

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[1] H. Gilman and D. Wittenberg, *J. Am. Chem. Soc.*, **79**, 6339 (1957).

[2] D. Wittenberg, H. A. McNinch, and H. Gilman. *ibid.*, **80**, 5418 (1958).

[3] H. Gilman and E. A. Zuech, *Chem. Ind.* (London), 1227 (1958).

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

[5] H. Gilman and E. A. Zuech, *J. Org. Chem.*, **26**, 3481 (1961).

[6] C. Tamborski, New York Academy of Sciences, International Symposium on Organometallic Chemistry, June 1964.

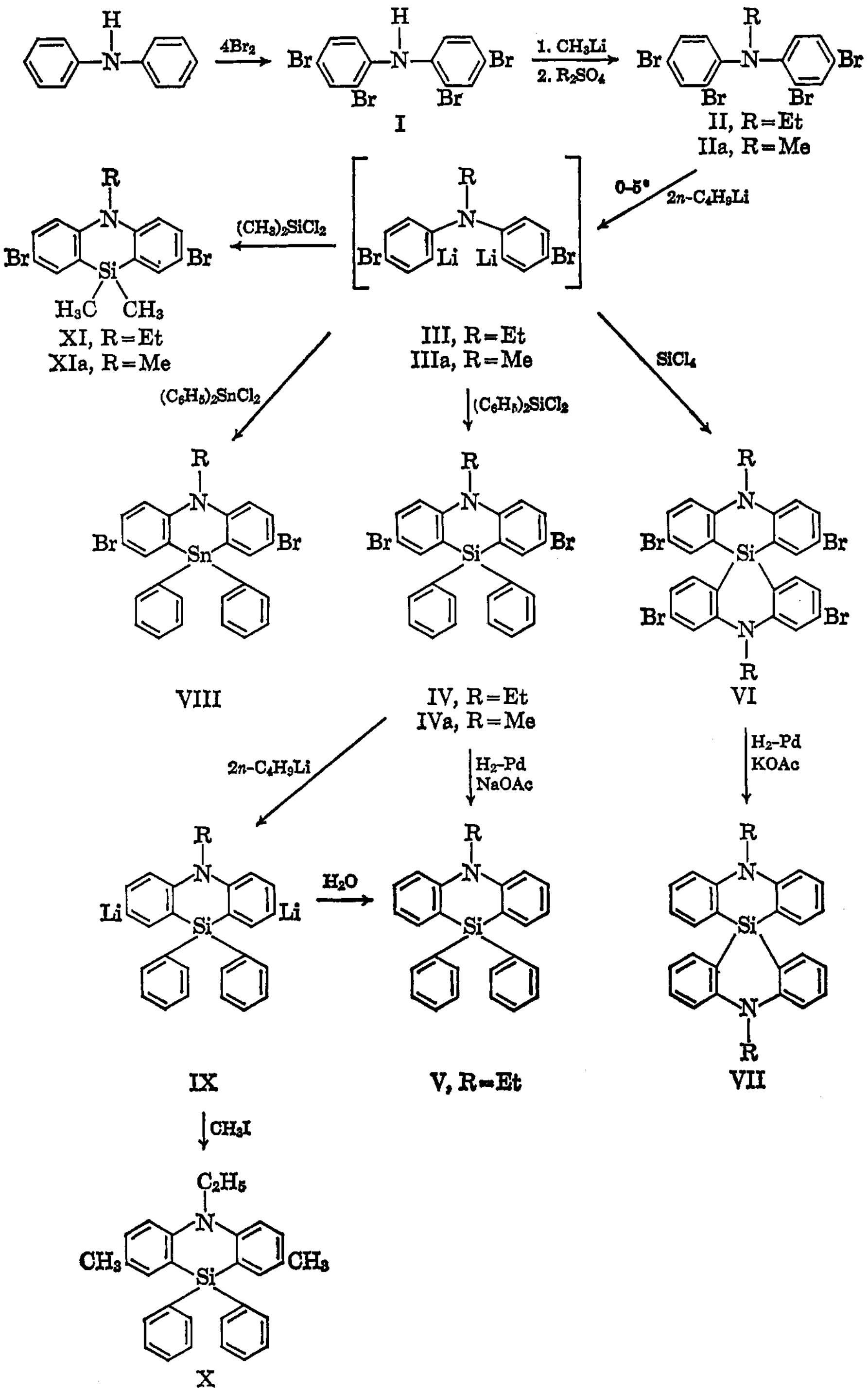
[7] G. Baum, H. A. Lloyd, and C. Tamborski, *J. Org. Chem.*, **29**, 3410 (1964).

[8] Melting points and boiling points are uncorrected. Organometallic reactions were run under a blanket of oxygen-free, dry nitrogen. Color Test I for aryllithium, and Color Test II for alkyllithium were applied throughout to determine reaction completion.

[9] A. W. Hoffmann, *Ann.*, **132**, 166 (1872).

[10] H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **55**, 1252 (1933).

SCHEME I



mole) was added. After 20 hr. of reflux, water hydrolysis of excess diethyl sulfate, toluene extraction, and cooling, 20 g. of product was obtained. The mother liquor was partially evaporated to yield an additional 28 g. of solid. The combined product was recrystallized three times from dimethylformamide to yield 20.1 g. (39%) of 2,2′,4,4′-tetrabromo-N-ethyldiphenylamine (II), m.p. 136.5–138.5°.

Anal. Calcd. for $C_{14}H_{11}Br_4N$: Br, 62.30. Found: Br, 62.41.

2,8-Dibromo-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (IV).—A suspension of 2,2′,4,4′-tetrabromo-N-ethyldiphenylamine (10.26 g., 0.02 mole) in dry diethyl ether was cooled to 0°; butyllithium (31.2 ml., 0.04 mole) was added dropwise. After 1 hr. at 0° the suspended material slowly went into solution as 4,4′-dibromo-N-ethyl-2,2′-dilithiodiphenylamine (III). An ether solution of diphenyldichlorosilane (5.07 g., 0.02 mole) was added dropwise. The temperature was raised to 22° in 15 min. and maintained there for 3 hr. Color Test I[11] for aryl or aliphatic lithium was negative. Neutralization with dilute sulfuric acid, water washing of the organic layer, and distillation of the ether yielded 16.2 g. of brown solid, m.p. 147–195°. Recrystallization from *n*-butyl alcohol and then from acetone yielded rhombic crystals of pure 2,8-dibromo-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline, m.p. 206.5–207.5°, $\lambda_{\max}^{CHCl_3}$ 223 mμ (ϵ 41,600).[12] A mixture melting point with an authentic sample of 2,8-dibrominated V showed no depression of the melting point.

Anal. Calcd. for $C_{26}H_{21}Br_2NSi$: Br, 29.87. Found: Br, 29.47.

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

[12] E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press Inc., New York, N. Y., 1955, p. 135.

2,2′,4,4′-Tetrabromo-N-methyldiphenylamine (IIa).—N-Methyldiphenylamine[13] (50 g., 0.273 mole) was dissolved in a mixture of carbon tetrachloride and chloroform (50:50 v./v., 1100 ml.) and a solution of N-bromosuccinimide (200 g., 1.125 moles) was added slowly at room temperature in 20 hr. The mixture was water washed and dried over magnesium sulfate, and the solvent was removed. The yield was 126 g. of solid, m.p. 143–146°. Recrystallization from hot Skellysolve C afforded an 83% yield of pure 2,2′,4,4′-tetrabromo-N-methyldiphenylamine (IIa), m.p. 142–144°, $\lambda_{max}^{CHCl_3}$ 291 mμ (ε 14,500).

Anal. Calcd. for $C_{13}H_9Br_4N$: C, 31.3; H, 1.82; Br, 64.2. Found: C, 31.6; H, 1.66; Br, 64.3.

2,8-Dibromo-5-methyl-10,10-diphenyl-5,10-dihydrophenazasiline (IVa).—To an ether (300 ml.) solution of 2,2′,4,4′-tetrabromo-N-methyldiphenylamine (37.4 g., 0.075 mole) was added an ether solution of *n*-butyllithium (175 ml., 0.12 mole). After addition of dichlorodiphenylsilane (18.9 g.) in ether (90 ml.), the reaction was found to be complete in 22 hr. at −5 to 0°. The solution was washed with water and the organic layer was dried over anhydrous sodium sulfate. Solid 2,8-dibromo-5-methyl-10-diphenyl-5,10-dihydrophenazasiline recovered on removal of the solvent weighed 30.6 g., m.p. 170–198°. The product recrystallized from *n*-butyl alcohol, m.p. 200–202°, $\lambda_{max}^{CHCl_3}$ 221 mμ (ε 33,200).

Anal. Calcd. for $C_{15}H_{19}Br_2NSi$: Br, 30.7. Found: Br, 30.7.

2,8-Dibromo-5-ethyl-10,10-dimethyl-5,10-dihydrophenazasiline (XI).—To a slurry of 2,2′4,4′-tetrabromo-N-ethyldiphenylamine (II, 25.6 g., 0.5 mole) in 175 ml. of dry ether at −5 to 0° was added ethereal *n*-butyllithium (6.4 g., 0.10 mole). To the resulting dilithio intermediate (III) was added dimethyldichlorosilane (6.4 g., 0.05 mole) at 0–5°. After 20 hr. the reaction mixture was water washed and dried over anhydrous sodium sulfate, and the ether was distilled, leaving 19.0 g. of crude solid product. Recrystallization from isopropyl alcohol yielded pure 2,8-dibromo-5-ethyl-10,10-dimethyl-5,10-dihydrophenazasiline (XI), m.p. 132.5–134°, $\lambda_{max}^{CHCl_3}$ 295 mμ (ε 20,500).

Anal. Calcd. for $C_{15}H_{17}Br_2NSi$: Br, 38.9. Found: Br, 38.9.

2,8-Dibromo-5,10,10-trimethyl-5,10-dihydrophenazasiline (XIa).—The same procedure as for the 5-ethyl derivative XI was followed to produce the above product, m.p. 148–149°.

Anal. Calcd. for $C_{14}H_{15}Br_2NSi$: C, 45.4; H, 3.81; Br, 40.02. Found: C, 45.25; H, 3.96; Br, 40.03.

5-Ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (V).—Hydrogenation of 2,8-dibromo-5-ethyl-10,10-diphenylphanazasiline (535 mg., 0.001 mole) in benzene (3 ml.) with 5% palladium on charcoal (250 mg.) and sodium acetate (500 mg.) was carried out at 25° for 4 hr. at 35- to 40-p.s.i.g. pressure. The charge was filtered, water washed, and dried with anhydrous sodium sulfate. The crude product upon removal of benzene weighed 377 mg., m.p. 115–125°, and was bromine free. Recrystallization of 353 mg. of crude product from ethanol yielded pure 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (310 mg., 88% yield), m.p. 122–125°. Mixtures with authentic 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline showed no depression of the melting point.

5-Methyl-10,10-diphenyl-5,10-dihydrophenazasiline (Va).—A solution of 2,8-dibromo-5-methyl-10,10-diphenylphenazasiline (1.3 g., 0.0025 mole) in a mixture of benzene (10 ml.) and ethanol (10 ml.) was hydrogenated with potassium acetate (0.612 g., 0.0063 mole) and 5% palladium on charcoal (0.1 g.) under 40-p.s.i.g. pressure for 72 hr. Work-up similar to Va yielded a crude product weighing 1.08 g. Recrystallization from ethyl acetate and then Skellysolve B afforded pure 5-methyl-10,10-diphenyl-5,10-dihydrophenazasiline, m.p. 186–188°. This agrees with the compound reported by Gilman.[1,2]

2,8-Dibromo-5-ethyl-10,10-diphenyl-5,10-dihydrophenazastanine (VIII).—In the usual manner, 2,2′,4,4′-tetrabromo-N-ethyldiphenylamine (25.6 g., 0.05 mole) in diethyl ether (150 ml.) was first treated with ethereal *n*-butyllithium (159 ml., 0.10 mole) at 0°. After Color Test II[14] was negative, indicating complete reaction of *n*-butyllithium, a solution of diphenyltin dichloride (18.9 g., 0.055 mole) in diethyl ether (50 ml.) was added. After overnight reaction at 25°, the reaction mixture was water washed and dried with anhydrous sodium sulfate, and the crude solid obtained after removal of solvent was purified by chromatography on alumina, 39.3% yield, m.p. 177–178°.

Anal. Calcd. for $C_{26}H_{21}Br_2NSn$: C, 50.0; H, 3.38; Br, 25.5. Found: C, 50.5; H, 3.40; Br, 25.1.

2,8-Dimethyl-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (X).—To a suspension of 42.8 g. (0.08 moles) of the dibromosiline IV in 350 ml. of ether at 10° was added a total of 0.21 mole of ethereal *n*-butyllithium. A clear solution was first obtained, and then a precipitate separated. After 2 hr. the interconversion reaction was complete and 35.2 g. (0.25 mole) of methyl iodide in ether was added. The mixture was stirred for 16 hr. to complete the reaction. After hydrolysis and neutralization with acid, the solid product was extracted with benzene, and the solution was evaporated to give 32 g. of crude crystals, m.p. 147–156°. After chromatography on alumina and recrystallization from hexane, 16.1 g. (50%) of X was obtained, m.p. 162.5–163°, $\lambda_{max}^{CHCl_3}$ 223 mμ (ε 36,600).

Anal. Calcd. for $C_{28}H_{27}NSi$: C, 83.94; H, 6.68. Found: C, 83.76; H, 6.43.

5-Ethyl-10-,10-diphenyl-5,10-dihydrophenazasiline (V).—A suspension of 2,8-dibromo-5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline (IV, 10.7 g., 0.02 mole) in dry diethyl ether (150 ml.) was slowly treated with ethereal *n*-butyllithium (57.3 ml., 0.055 mole) at 0°. After 1.5 hr. at 10–15° tests indicated complete interconversion of lithium for bromine. The suspension was poured on 400 g. of ice and water and neutralized with dilute sulfuric acid, and the ether layer was washed with water. Crude product obtained by distillation of solvent was bromine free. After five recrystallizations from isopropyl alcohol, 2.0 g. of product, m.p. 120.5–122°, was obtained. Mixture with an authentic sample of 5-ethyl-10,10-diphenyl-5,10-dihydrophenazasiline showed no depression of the melting point.

2,2′,8,8′-Tetrabromo-5,5′-diethyl-10,10′-spirobi(5,10-dihydrophenazasiline) (VI).—To a suspension of 2,2′,4,4′-tetrabromo-N-ethyldiphenylamine (115.2 g., 0.0025 mole) in diethyl ether (675 ml.) was slowly added 0.45 mole of ethereal *n*-butyllithium at −5 to 0° during 50 min.; this was held for 1.25 hr. A solution of silicon tetrachloride (19.6 g., 0.1152 mole) in diethyl ether (90 ml.) was then added at −30° in 0.5 hr. The reaction mixture was held at 25° for 19 hr. and then mixed with water. The white solid was filtered, washed with water, dried, and upon recrystallization from diethyl ether yielded pure VI, 62.0 g. (75.1% yield), m.p. 275–276.5°, $\lambda_{max}^{CHCl_3}$ 321 mμ (ε 21,300).

Anal. Calcd. for $C_{28}H_{22}Br_4NSi$: C, 45.8; H, 3.02. Found: C, 45.5; H, 3.46.

5,5′-Diethyl-10,10′-spirobi(5,10-dihydrophenazasiline) (VII).—Debromination of 2,2′,8,8′-tetrabromo-10,10′-diethylspirobiphenylphenazasiline (7.34 g., 0.01 mole) in benzene (100 ml.) was accomplished, using a solution of potassium acetate (2.9 g., 0.06 mole in 60 ml. of ethanol), 5 g. of 5% palladium on charcoal, and 40-p.s.i.g. pressure at 60°, in 1.75 hr. After removal of catalyst, water wash, and solvent distillation, bromine-free crude product was obtained, weighing 4.0 g. Ethyl acetate recrystallization yielded 3.4 g. (81%) of 5,5′-diethyl-10,10′-spirobi(5,10-dihydrophenazasiline), m.p. 214–216°, $\lambda_{max}^{CHCl_3}$ 223 mμ (ε 55,120). This agrees with the compound obtained by Gilman and Zeuch,[3] m.p. 215.5–217°.

Acknowledgment.—Analytical results were obtained by Mr. R. N. Boos and Miss L. E. May. The ultraviolet spectra were run by Mr. A. Kalowsky. Special thanks are due Dr. F. M. Meigs for his organizational support.

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Tetracyano-*p*-phenylenediamine

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In the course of studies aimed at the synthesis of hexacyanobutadiene[1] from 1,1,2,2-tetracyanoethane[2]

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