[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

# Group IV-B Element Analogs of 5,10-Dihydroacridine

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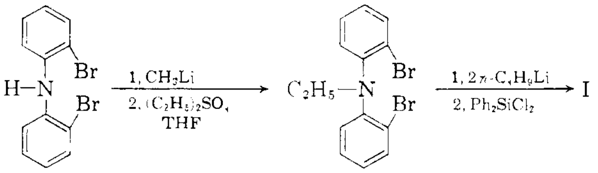
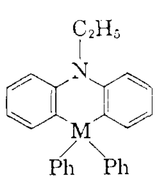
2,2′-Dibromodiphenylamine was successfully converted to the N-ethyl derivative. From the reaction of N-ethyl-2,2′-dilithiodiphenylamine with dichlorodiphenylsilane, diphenylgermanium dichloride, diphenyltin dichloride and diphenyllead dibromide there were obtained 5 ethyl-5,10-dihydro-10,10-diphenylphenazasiline, 5-ethyl-5,10-dihydro-10,10-diphenylphenazagermine, 5-ethyl-10,10-dihydro-10,10-diphenyl-5*H*-phenazastannine and 5-ethyl-10,10-dihydro-10,10-diphenyl-5*H*-phenazaplumbine, respectively. 5,5′-Diethyl-10,10′-spirobi-(5,10-dihydrophenazasiline), 5,5′-diethyl-10,10′-spirobi-(5,10-dihydrophenazagermine) and 5,5′-diethyl-10,10′-spirobi-(10,10-dihydro-5*H*-phenazastannine) were similarly prepared from the corresponding tetrachlorides. An attempt to prepare 5,5′-diethyl-10,10′-spirobi-(10,10-dihydro-5*H*-phenazaplumbine) from lead(II) chloride was unsuccessful.

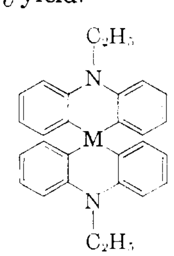
Silicon analogs of 5,10-dihydroacridine, 5,10-dihydro-10,10-diphenylphenazasilane[1] and 5-ethyl-5,10-dihydro-10,10-diphenylphenazasiline (I) were first prepared by the extended heating of diphenylsilane with phenothiazine and 10-ethylphenothiazine,[2] respectively. However, this method of synthesis suffers from the diadvantages of difficult work-ups and very low yields. Inasmuch as these compounds promise to be of significant value in high temperature lubricants, it was of interest to devise a better method of synthesis. N-Ethyl-2,2′-dilithiodiphenylamine[3] was found to react with dichlorodiphenylsilane to give a very much improved yield of I. The superiority of this method, in addition to the higher yield, lies in the ease of work-up and in its versatility. Reaction of the dilithium compound with various halides of Group IV-B elements afforded several new heterocyclic types confirming one aspect of the broad applicability of the synthesis.



2,2′-Dibromodiphenylamine was prepared by the Chapman rearrangement as described in the elegant studies of Jones and Mann.[4] Attempts by these workers to prepare the N-methyl derivative were unsuccessful. To facilitate N-alkylation, 2,2′-dibromodiphenylamine was converted to the N-lithio derivative by treatment with methyllithium. However, reaction of the N-lithio compound with a refluxing ethereal solution of diethyl sulfate failed to produce the N-ethyl derivative. When the same reaction was carried out in refluxing tetrahydrofuran (THF), the N-ethyl derivative was obtained in an 83% yield. A similar reaction employing a toluene–ether solution heated to 65°, the reflux temperature of tetrahydrofuran, gave only partial N-alkylation thus indicating the importance of the tetrahydrofuran. N-Ethyl-2,2′-dilithiodiphenylamine was prepared by a halogen–metal interconversion reaction between the N-ethyl-2,2′-dibromo compound and two equivalents of *n*-butyllithium. Jones and Mann[4] had previously found that halogen–metal interconversion of 2,2′-dibromodiphenylamine with *n*-butyllithium followed by carbonation gave 2,2′-dicarboxydiphenylamine in 84% yield.



M =
I, Si
II, Ge
III, Sn
IV, Pb



M =
V, Si
VI, Ge
VII, Sn
VIII, Pb

Reaction of equal molar quantities of dichlorodiphenylsilane and N-ethyl-2,2′-dilithiodiphenylamine afforded I, which was shown to be identical with an authentic sample obtained from 5-ethylphenothiazine and diphenylsilane.[2] Analogously, diphenylgermanium dichloride, diphenyltin dichloride and diphenyllead dibromide gave 5-ethyl-5,10-dihydro-10,10-diphenylphenazagermine (II), 5-ethyl-10,10-dihydro-10,10-diphenyl-5*H*-phenazastannine (III) and 5-ethyl-10,10-dihydro-10,10-diphenyl-5*H*-phenazaplumbine (IV), respectively. The yields of the compounds in this series were I, 49.3%; II, 52.4%; III, 33.7%; and IV, 26%.

Treatment of silicon tetrachloride with two equivalents of N-ethyl-2,2′-dilithiodiphenylamine gave a 44.4% yield of 5,5′-diethyl-10,10′-spirobi-(5,10-dihydrophenazasiline) (V). In a similar manner, the dilithium derivative was treated with germanium tetrachloride and with stannic chloride to give 5,5′-diethyl-10,10′-spirobi-(5,10-dihydrophenazagermine) (VI) and 5,5′-diethyl-10,10′-spirobi-(10,10-dihydro-5*H*-phenazastannine) (VII) in yields of 18.1 and 28.5%, respectively. An attempt to prepare the corresponding lead compound, 5,5′-diethyl-10,10′-spirobi-(10,10-dihydro-5*H*-phenazaplumbine) (VIII), by treating anhydrous lead-(II) chloride with one equivalent of N-ethyl-2,2′-dilithiodiphenylamine, was unsuccessful.

All of the infrared spectra of these compounds determined as carbon disulfide solutions showed

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(1) The names and the numbering systems used herein were recommended by Dr. L. T. Capell of *Chemical Abstracts*. Previously the phenazasiline derivatives had been named without using the 5,10-dihydro nomenclature.

(2) H. Gilman and D. Wittenberg, THIS JOURNAL, **79**, 6339 (1957); D. Wittenberg, H. A. McNinch and H. Gilman, *ibid.*, **80**, 5418 (1958).

(3) For a preliminary account, see H. Gilman and E. A. Zuech, *Chemistry & Industry*, 1227 (1958).

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

absorption bands at 7.4, 7.6, 7.9 and 8.2$\mu$. These bands were more pronounced in the silicon and germanium compounds. The characteristic band for *o*-disubstituted benzene at 13.2–13.3$\mu$ was present in all of the spectra; while, the 10,10-diphenyl derivatives also had the mono-substitution absorption. In addition the characteristic absorption bands of the Group IV-B elements linked to benzene were present in the spectra.

## Experimental[5]

**N-Ethyl-2,2'-dibromodiphenylamine.**—A solution of 10 g. (0.0306 mole) of 2,2'-dibromodiphenylamine[4] cooled in an ice-bath was treated with 0.035 mole of an ethereal solution of methyllithium, and allowed to stir for 30 minutes. Subsequently, 7.7 g. (0.05 mole) of freshly distilled diethyl sulfate in 100 ml. of tetrahydrofuran was added. The ether was removed by distillation until the temperature reached 64°. This solution was heated at reflux for 15 hours, and then hydrolyzed by pouring into iced water. The organic solution was separated, and the aqueous layer extracted with ether and discarded. After drying with anhydrous sodium sulfate, the solvents were distilled and the resulting material distilled at reduced pressure to give 8.99 g. (83%) of colorless liquid, b.p. 131–133° (0.04 mm.), which solidified upon standing. A portion was recrystallized from petroleum ether (b.p. 60–70°) giving colorless crystals, m.p. 72–74°.

*Anal.* Calcd. for $C_{14}H_{13}Br_2N$: N, 3.97. Found: N, 4.02, 3.87.

**5-Ethyl-5,10-dihydro-10,10-diphenylphenazasiline.**—To 5.05 g. (0.014 mole) of N-ethyl-2,2'-dibromodiphenylamine in 50 ml. of ether cooled in an ice-bath, there was added 0.028 mole of *n*-butyllithium. After stirring under these conditions for 1 hour, Color Test II[6] was negative. The solution was treated with 3.60 g. (0.014 mole) of dichlorodiphenylsilane in 100 ml. of ether. The reaction mixture was stirred for 28 hours at room temperature, before Color Test I[7] was negative. Hydrolysis was carried out by pouring into ice water and the organic layer separated. The aqueous layer was extracted with ether and discarded. The combined organic solution was dried with anhydrous sodium sulfate and the ether removed by evaporation under an air-jet. The resulting solid was taken up in petroleum ether (b.p. 60–70°) to give 3.11 g. of colorless crystals, m.p. 118–121°. Recrystallization from the same solvent gave 2.66 g. (49.3%) of 5-ethyl-5,10-dihydro-10,10-diphenylphenazasiline, m.p. 121–123°, identified by mixed melting point with an authentic sample and by comparison of infrared spectra.[2]

**5-Ethyl-5,10-dihydro-10,10-diphenylphenazagermine.**—A solution of N-ethyl-2,2'-dilithiodiphenylamine, prepared from 5.33 g. (0.015 mole) of N-ethyl-2,2'-dibromodiphenylamine and 0.03 mole of *n*-butyllithium in 50 ml. of ether, was treated with 4.46 g. (0.015 mole) of diphenylgermanium dichloride in 50 ml. of ether, and the reaction mixture was refluxed for 16 hours. Subsequently, 50 ml. of dry toluene was added, the ether distilled, and the toluene solution refluxed for 2 hours. Color Test I[7] was negative and hydrolysis was carried out with 50 ml. of water. The organic layer was separated, dried over sodium sulfate and evaporated under an air-jet. The resulting solid was recrystallized twice from petroleum ether (b.p. 60–70°) giving 3.47 g. (52.4%) of colorless crystals, m.p. 119–121°. An additional recrystallization raised the melting point to 120–121°.

*Anal.* Calcd. for $C_{26}H_{23}GeN$: Ge, 17.20; N, 3.32. Found: Ge, 17.09, 17.51; N, 3.25, 3.24.

**5-Ethyl-10,10-dihydro-10,10-diphenyl-5*H*-phenazastannine.**—An ethereal solution containing 0.02 mole of N-ethyl-2,2'-dilithiodiphenylamine was allowed to react with 6.87 g. (0.02 mole) of diphenyltin dichloride in 50 ml. of ether as described in the preceding experiments. After hydrolysis and the usual work-up, the resulting material was recrystallized from petroleum ether (b.p. 60–70°) to give 3.15 g. (33.7%) of colorless crystals, m.p. 116–119°. The analytical sample melted at 117–119°.

*Anal.* Calcd. for $C_{26}H_{23}NSn$: Sn, 25.36. Found: Sn, 25.62, 25.80.

**5-Ethyl-10,10-dihydro-10,10-diphenyl-5*H*-phenazaplumbine.**—A suspension of 7.82 g. (0.015 mole) of diphenyllead dibromide in 150 ml. of ether was added to a cold solution of 0.015 mole of N-ethyl-2,2'-dilithiodiphenylamine in 50 ml. of ether. The ether solution was refluxed for 16 hours, 50 ml. of toluene was added, and the ether distilled. After refluxing for 2 hours, Color Test I[7] was negative and the reaction mixture was hydrolyzed. Work-up was carried out in the usual manner and the resulting material was crystallized twice from petroleum ether (b.p. 60–70°) giving 2.18 g. (26%) of colorless crystals, m.p. 121–122.5°. Another recrystallization raised the melting point to 121.5–123°.

*Anal.* Calcd. for $C_{26}H_{23}NPb$: C, 56.09; H, 4.16; N, 2.52. Found: C, 56.50, 56.29; H, 4.34, 4.43; N, 2.50, 2.39.

**5,5'-Diethyl-10,10'-spirobi-(5,10-dihydrophenazasiline).**—To a solution of 10.65 g. (0.03 mole) of N-ethyl-2,2'-dibromodiphenylamine in 100 ml. of ether cooled in an ice-bath, there was added 0.06 mole of *n*-butyllithium over a period of 10 minutes. After stirrring for 40 minutes, 2.55 g. (0.015 mole) of freshly distilled silicon tetrachloride in 100 ml. of ether was added, and the reaction mixture stirred for 2.5 hours at room temperature. The ether solution was refluxed for 18 hours, 100 ml. of dry toluene was added, and then the ether distilled. The resulting toluene suspension was refluxed for 2 hours before Color Test I[7] was negative. After hydrolysis by pouring into cold water, the aqueous layer was separated, extracted with ether, and discarded. The combined organic layer was dried with anhydrous sodium sulfate and evaporated under an air-jet. The resulting material was taken up in ethyl acetate giving 3.19 g. of colorless needles, m.p. 210–214°. After two recrystallizations from the same solvent, there was obtained 2.78 g. (44.4%) of colorless needles, m.p. 215.5–217°.

*Anal.* Calcd. for $C_{28}H_{26}N_2Si$: Si, 6.71. Found: Si, 6.75, 6.63.

**5,5'-Diethyl-10,10'-spirobi-(5,10-dihydrophenazagermine).**—To a solution of 0.03 mole of N-ethyl-2,2'-dilithiodiphenylamine in 150 ml. of ether, there was added 3.21 g. (0.015 mole) of germanium tetrachloride in 50 ml. of ether, and the reaction mixture was refluxed for 16 hours. Subsequently, 100 ml. of dry toluene was added, the ether distilled, and the toluene suspension heated at reflux for 4 hours. After hydrolysis, ether was added, and the organic layer was separated and dried. The organic layer was evaporated and the resulting material crystallized from ethyl acetate to give 1.76 g. of colorless solid, m.p. 205–211°. Recrystallization from ethyl acetate gave 1.26 g. (18.1%) of colorless needles, m.p. 212–214°.

*Anal.* Calcd. for $C_{28}H_{26}GeN_2$: Ge, 15.68. Found: Ge, 15.58, 15.76.

**5,5'-Diethyl-10,10'-spirobi-(10,10-dihydro-5*H*-phenazastannine).**—A solution of 3.90 g. (0.015 mole) of anhydrous stannic chloride was added to 0.03 mole of N-ethyl-2,2'-dilithiodiphenylamine in 150 ml. of ether and the ethereal solution was heated at reflux for 17 hours. Fifty ml. of dry toluene was added, the ether distilled, and the toluene suspension refluxed for 3 hours. Hydrolysis and work-up were carried out in the usual manner, and the resulting material was recrystallized twice from ethyl acetate to give 2.18 g. (28.5%) of colorless needles, m.p. 209–210.5°. An additional recrystallization raised the melting point to 210–211°.

*Anal.* Calcd. for $C_{28}H_{26}N_2Sn$: N, 5.50; Sn, 23.31. Found: N, 5.34, 5.52; Sn, 23.78, 23.70.

**5,5'-Diethyl-10,10'-spirobi-(10,10-dihydro-5*H*-phenazaplumbine) (Attempted).**—A suspension of 8.34 g. (0.03 mole) of lead(II) chloride in 200 ml. of ether was added to an ethereal solution of 0.03 mole of N-ethyl-2,2'-dilithiodiphenylamine. The formation of a black precipitate was noted during the addition. The ethereal solution was refluxed for 22 hours, and, subsequently, 50 ml. of dry toluene was added. After removing the ether by distillation, the toluene suspension was refluxed for 2 hours. The reaction mixture was hydrolyzed with water, ether was added, and

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[5] All reactions involving organometallic compounds were carried out in an atmosphere of dry, oxygen-free nitrogen, and all melting and boiling points are uncorrected.

[6] H. Gilman and J. Swiss, THIS JOURNAL, **62**, 1847 (1940).

[7] H. Gilman and F. Schulze, *ibid.*, **47**, 2002 (1925).

the mixture filtered. The organic solution was separated and the aqueous layer extracted with ether. The combined organic solution was dried with anhydrous sodium sulfate and distilled. The remaining brown thick oil was treated in various ways, but none of the desired compound could be isolated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

# Condensed Cyclobutane Aromatic Compounds. XI. Benzo[1,2:4,5]dicyclobutene

BY M. P. CAVA, A. A. DEANA AND K. MUTH

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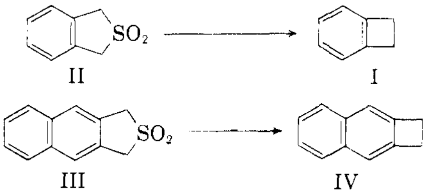
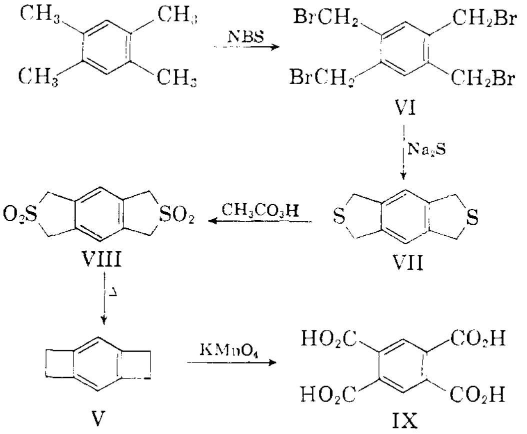
Benzo[1,2:4,5]dicyclobutene (V) has been synthesized from $\alpha,\alpha',\alpha'',\alpha'''$-tetrabromodurene *via* the intermediary disulfone VIII. The hydrocarbon V is the first example of a system containing more than one cyclobutane ring fused to a single aromatic nucleus.

A novel synthesis of benzocyclobutene (I) consists of the thermal extrusion of sulfur dioxide from the cyclic sulfone 1,3-dihydroisothianaphthene-2,2-dioxide (II).[1] A subsequent application of this reaction was found in the pyrolysis of sulfone III to naphtho[b]cyclobutene (IV).[2] The use of the sulfone pyrolysis method has now been extended to the synthesis of benzo[1,2:4,5]dicyclobutene(V), the first known system containing an aromatic nucleus condensed to two cyclobutane rings.



$\alpha,\alpha',\alpha'',\alpha'''$-Tetrabromodurene(VI), prepared by treatment of durene with N-bromosuccinimide,[3] reacted with sodium sulfide to give, in 48% yield 1,3,5,7-tetrahydrobenzo[1,2-c:4,5-c′]dithiophene(VII), m.p. 213–217°. Peracetic acid oxidation of the disulfide VII afforded the corresponding disulfone, tetrahydrobenzo[1,2-c:4,5-c′]dithiophene-2,-2,6,6-tetroxide(VIII). The white crystalline disulfone VIII possessed no definite melting point below 400°, but slowly decomposed to a black powder on strong heating. However, when small samples of the disulfone, diluted with copper powder, were heated at 320° in a low pressure nitrogen atmosphere a volatile hydrocarbon $C_{10}H_{10}$ sublimed out in 20% yield. Passage of the pyrolysate vapors through a Nichrome coil heated to dull red heat[1] increased the yield to 40%. This substance, m.p. 101°, which crystallized in white prisms from methanol, was ascribed the structure benzo[1,2:4,5]dicyclobutene (V). In accord with this formulation, oxidation of V with potassium permanganate yielded pyromellitic acid (IX), isolated as the dianhydride.

A striking manifestation of the extraordinary strain present in benzo[1,2:4,5]dicyclobutene was found in its ultraviolet absorption spectrum. A comparison of the ultraviolet spectrum of V with that of durene (Fig. 1) shows a very appreciable bathochromic shift on going from durene to V. In addition, the extinction coefficients of the maxima of V in the 270–290 $m\mu$ region are almost ten times greater than the corresponding maxima of durene. Clearly the distortion effect caused by two fused four-membered rings upon the ultraviolet absorbtion of an aromatic nucleus is considerably more pronounced than the corresponding effect of a single fused cyclobutane ring.[2,4]



An investigation of the chemistry of benzo[1,2:4,5]dicyclobutene is in progress in our laboratory, and the results will be discussed in a subsequent paper of this series.

**Acknowledgments.**—We should like to thank the National Science Foundation for a grant in support of this work. We are grateful also to Mr. John Stone of "Chemical Abstracts" for suggestions concerning nomenclature.

## Experimental[5]

**1,3,5,7-Tetrahydrobenzo[1,2-c:4,5-c′]dithiophene(VII).**—$\alpha,\alpha',\alpha'',\alpha'''$-Tetrabromodurene[3] (9.0 g., 0.02 mole) was added to a mixture of sodium sulfide monohydrate (10 g.,

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[1] M. P. Cava and A. A. Deana, THIS JOURNAL, **81**, 4266 (1959).

[2] M. P. Cava and R. L. Shirley, *ibid.*, **82**, 654 (1960).

[3] W. Ried and H. Bodem, *Chem. Ber.*, **89**, 2328 (1956).

[4] M. P. Cava and D. R. Napier, THIS JOURNAL, **80**, 2255 (1958).

[5] Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected unless stated otherwise.