a 12-ft β,β'-oxydipropionitrile (25%) column at 60°. The experiment was carried out in duplicate on two separate occasions.

Triplet Counting. Singlet–triplet crossover efficiency experiments were carried out using the technique of Lamola and Hammond. This determination was done in duplicate, on two separate occasions. On the first occasion, a benzene solution 0.60 *M* in benzophenone and 0.10 *M* in *cis*-piperylene was irradiated for 1 hr with 3130-A light on the "merry-go-round," and the extent of isomerization to the *trans* isomer was measured using the β,β'-oxydipropionitrile column at 60°. A benzene solution 0.33 *M* in cyclopentenone and 0.10 *M* in *cis*-piperylene was also irradiated under the same conditions and for the same length of time. The extent of isomerization thus produced was compared with that obtained using the benzophenone solution. On the second occasion, the solutions were 0.30 *M* in benzophenone, 0.50 *M* in cyclopentenone, and 0.20 *M* in *cis*-piperylene.

Analysis of By-Product III. III was trapped from the vpc outlet, using the Carbowax 20M column at ~200°. The material thus obtained was then subjected to nuclear magnetic resonance analysis on a Varian A-60A spectrometer. Infrared analysis was carried out with a Perkin-Elmer Model 421 infrared spectrophotometer. Ultraviolet spectra were taken using a Perkin-Elmer Model 202 ultraviolet spectrophotometer. Carbon–hydrogen analysis was done by Eastman Kodak Research Laboratories, Rochester, N. Y. Mass spectral data were obtained through the courtesy of N. J. Turro at Columbia University.

Irradiation on Silica Gel. The behavior of cyclopentenone on silica gel was studied using slurries produced by intimate mixing of activated silica gel and solutions of cyclopentenone in cyclohexane. These slurries were in general irradiated in ~100-ml lots on the Hanovia lamp. Since the slurry was placed in the outer jacket of the lamp which normally contained the solution filter (*vide supra*), the only light filtration employed in irradiation of slurries was that provided by a Pyrex filter which cut out all light below about 3000 A. After irradiation, the slurry was removed and extracted with a 1:1 mixture of methanol and chloroform. The combined washings and supernatant cyclohexane solution originally remaining above the slurry were concentrated at room temperature under aspirator pressure, by a factor of about 100. This resulting mixture was then analyzed as usual by vpc, using the Carbowax 20M column at 240°.

Extent of Adsorption of Cyclopentenone on Silica Gel. This value was measured by comparing the ultraviolet spectra of the original cyclopentenone solution with that of the supernatant liquid above a slurry produced by combination of 0.50 g of activated silica gel and 1.0 ml of cyclopentenone solution.

Irradiation of Oxygenated Cyclopentenone Solutions. Oxygen gas was continuously bubbled through a solution of cyclopentenone in cyclohexane throughout irradiation for 3 hr. The solution was kept cold by surrounding it with an ice bath. The composition of the resulting solution was then compared with that of a nonoxygenated one of the same concentration, by vpc. The Carbowax 20M column was used as usual.

Acknowledgments. We are indebted to Dr. N. J. Turro for obtaining the mass spectrum of III and to Dr. J. A. Leermakers for C and H analyses of III. We also thank Dr. G. W. Griffin for authentic samples of I and II. Financial support was provided by National Institutes of Health (Grant GM 13592-01) and the American Chemical Society Petroleum Research Fund. Finally, we wish to thank Professors G. S. Hammond and P. De Mayo for prepublication copies of their results.

Boron–Pyrazole Chemistry. III. Chemistry of Pyrazaboles

S. Trofimenko

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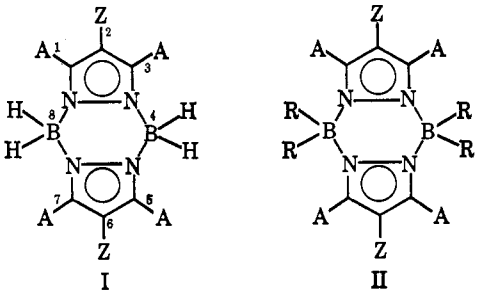
Received May 19, 1967

Abstract: Pyrazaboles react with halogens and with some active hydrogen compounds to yield 4,8-di- and 4,4,8,8-tetrasubstituted derivatives. Diverse C-substituted derivatives were prepared by direct synthesis with subsequent reactions at the functional groups. The wide variety of transformations carried out indicates considerable stability of the pyrazabole ring system.

Pyrazaboles (I) are a novel class of remarkably stable boron heterocycles.[1,2] In the first paper of this series the synthesis and properties of pyrazaboles of structures I and II were discussed. These compounds were obtained by the reaction of appropriately substituted pyrazoles with borane complexes or with trialkyl- or triarylboranes, respectively. Although widely applicable, such a synthetic approach, henceforth referred to as "direct synthesis," still had some limitations. For instance, some borane or pyrazole components were not readily available; and certain borane–pyrazole combinations were incompatible. Hence, additional routes to pyrazaboles containing diverse boron and carbon substituents were of interest. This paper is concerned with two aspects of pyrazabole chemistry: (a) substitution chemistry of pyrazaboles and (b) chemical transformations of functionally substituted pyrazaboles which maintain the intact ring system.



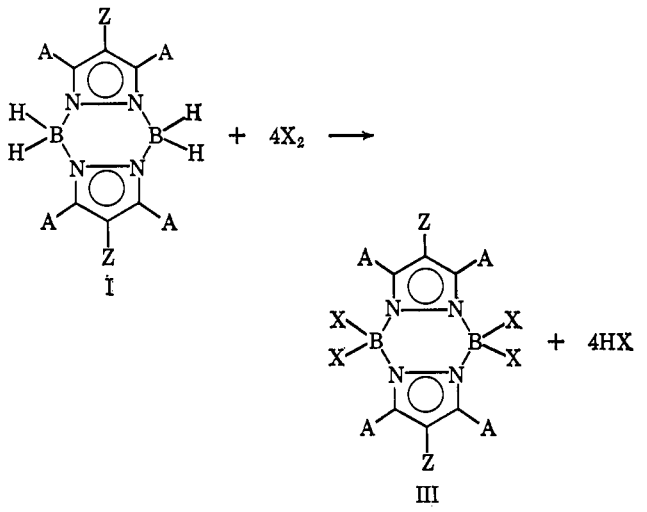
I II

R = alkyl, aryl
A = H, alkyl, aryl, halogen
Z = H, R, NO_2, CN, halogen

(1) S. Trofimenko, *J. Am. Chem. Soc.*, 88, 1842 (1966).
(2) S. Trofimenko, *ibid.*, 89, 3165 (1967).

Results and Discussion

Halogenation. When pyrazabole was stirred in a halocarbon solvent with excess chlorine, bromine, or iodine, a rapid and complete reaction resulted in the replacement of all four boron-bonded hydrogens and formation of 4,4,8,8-tetrahalopyrazaboles (III, A = Z = H), unaffected by either the hydrogen halide



I III

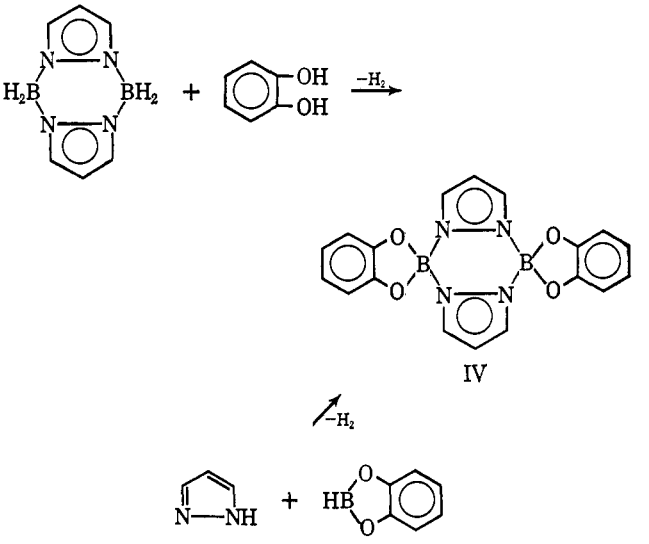
evolved or by excess halogen. The tetrachloro and tetrabromo derivatives were high-melting solids that could be sublimed *in vacuo* and recrystallized from organic solvents. The tetraiodo compound was relatively unstable and decomposed on storage. 4,4,8,8-Tetrafluoropyrazabole[3] was prepared in poor yield by the reaction of Me_3NBF_3 and pyrazole. The stability order of 4,4,8,8-tetrahalopyrazaboles is F > Cl > Br > I.

The structure of the tetrahalo compounds follows from H^1 nmr data which show retention of all the C-hydrogens and of their original symmetry, and the infrared spectra which display strong bands in the boron–halogen stretch region[4] with concurrent disappearance of the BH stretch. 4,4,8,8-Tetraalkylpyrazaboles were completely unaffected by chlorine or bromine.

Halogenation was a convenient way to obtain crystalline derivatives from low-melting pyrazaboles such as 2,6-diisopropylpyrazabole and 1,3,5,7-tetramethyl-2,6-dibutylpyrazabole, which are difficult to crystallize. It is noteworthy, however, that 2,6-bis(perfluoroisopropyl)pyrazabole gave under conditions of exhaustive chlorination only a dichloro compound. That it was the 4,8 rather than 4,4 derivative was inferred from its infrared spectrum which had a BH singlet around 2500 cm^{-1}.

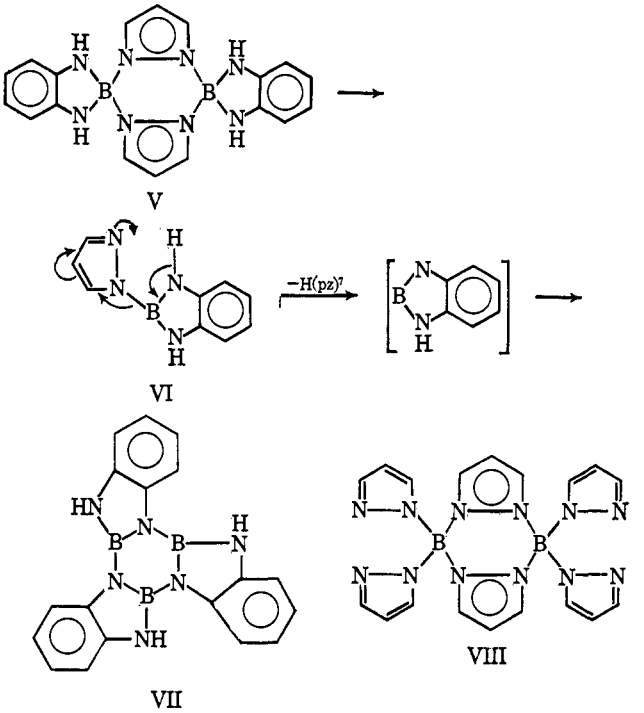
The 2,6 positions in pyrazaboles are remarkably inert toward halogenation. This is even more noteworthy if one considers that pyrazolium cation is halogenated at the 4 position quite readily,[5] and is compatible with a BR_2 group being a powerful electron withdrawer.

Reaction with Active Hydrogen Compounds. Heating pyrazabole with pyrocatechol produced the 4,4,8,8-bis(*o*-phenylenedioxy) derivative IV. This compound, too, had no BH bands in the infrared and had the normal pyrazabole-type doublet–triplet spectrum in the H^1 nmr. It was identical with the compound prepared by direct synthesis from *o*-phenylenedioxyborane. With phenol, 4,4,8,8-tetraphenoxypyrazabole was obtained. This compound was more readily hydrolyzed than the bis(*o*-phenylenedioxy) derivative.



IV

A different reaction course resulted when pyrazabole was heated with *o*-phenylenediamine. The product isolated was not the bis(N,N′-*o*-phenylenediamino) derivative, but rather the known[6] borazole derivative VII formed probably from cracking of pyrazabole V



V VI VII VIII

to fragments VI facilitated by electron release of the two amino nitrogens.

When pyrazabole was heated with excess pyrazole, 4,4,8,8-tetrakis(1-pyrazolyl)pyrazabole (VIII) was

(3) The fluorination of pyrazaboles and the chemistry of fluoropyrazaboles has been studied extensively by Dr. C. W. Heitsch; see Abstracts, 153rd National Meeting of the American Chemical Society, Miami, Fla., April 10–14, 1967, L109.

(4) W. Gerrard, "The Organic Chemistry of Boron," Academic Press Inc., New York, N. Y., 1961, p 226.

(5) Dr. J. K. Williams, private communication.

(6) R. J. Brotherton and H. Steinberg, *J. Org. Chem.*, **26**, 4632 (1961).

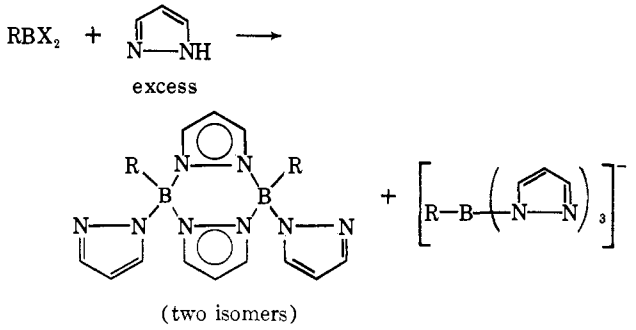
(7) (pz) stands for 1-pyrazolyl.

formed. The nmr spectrum of this compound shows an interesting example of a boron-bonded yet uncoordinated pyrazolyl group. It consists (in chloroform-*d*) of an asymmetric doublet at τ 2.32, a doublet (J = 2.4 cps, further split into doublets, J = 0.5 cps), a triplet (J = 2.6 cps), and a "triplet" consisting of two overlapping doublets (J = 2.4 and 1.7 cps), with relative intensities 4:2:1:2. The asymmetric doublet is assigned to overlapping 1,3,5,7 pyrazabole hydrogens and the 3 (or 5) pyrazole hydrogen, the second doublet to 3 (or 5) pyrazole hydrogen, the triplet to the 2,6 hydrogens, and the "triplet" to the 4 pyrazole hydrogen. The asymmetric doublet was resolved into two doublets, τ 2.37 (J = 2.6 cps) and 2.53 (J = 1.6 cps) (assigned to the 1,3,5,7 pyrazabole hydrogens and the 3 (or 5) pyrazole hydrogen, respectively), when the spectrum was determined in dimethyl sulfoxide. The other peaks were also shifted: the pyrazabole triplet was at τ 3.28, the other pyrazole doublet at τ 3.34, and the pyrazole "triplet" at τ 3.96.

Compound VIII could also be obtained in lower yield from pyrolysis of the free acid derived from tetrakis(1-pyrazolyl)borate ion or, among other products, from the reaction of boron trichloride with excess pyrazole.

When just 2 equiv of pyrazole was employed in the reaction with pyrazabole, 4,8-bis(1-pyrazolyl)pyrazabole was produced. It melted over a wide range, not inconsistent with it being a mixture of *cis* and *trans* isomers. No attempt was made to separate them. That this product contained 4,8 rather than 4,4 substituents was not only anticipated on steric grounds, but was also suggested by the presence of a BH singlet at 2470 cm^{-1} in the infrared spectrum and by proton nmr spectra which showed the typical pyrazabole A_2B pattern rather than the ABC pattern expected in the case of a 4,4-disubstituted pyrazabole. Another example of a 4,8-disubstituted pyrazabole was the 4,8-diphenyl derivative prepared by direct synthesis from the trimethylamine complex of phenylborane. This compound, too, melted over a relatively wide range suggestive of a *cis,trans* isomer mixture. Here, of course, there could be no question of the 4,8 location of the phenyl groups.

The reaction of RBX_2 and BX_3 compounds (X = Cl, Br) with excess pyrazole results in rapid replacement of all halogens by 1-pyrazolyl groups and produces a mixture of 4,8-di-R-4,8-di(pz)pyrazaboles and $RB(pz)_3^-$ as the pyrazolium salt. The order of reactivity



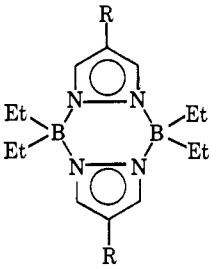
(two isomers)

in the BR_3 + Hpz reaction as a function of R is halogen > hydrogen > alkyl > aryl. Although this method gives a mixture of products and the yields are poor, it is simple and at times the only way to obtain a given pyrazabole or polypyrazolyl borate, their properties being sufficiently different to make separation possible.

In this fashion was obtained, for example, 4,8-diphenyl-4,8-bis(1-pyrazolyl)pyrazabole. It may be a single isomer, probably *trans*, judging by the sharpness of the melting point.

Chemistry of Functional Groups on the Pyrazabole Ring. The stability of the pyrazabole ring was investigated under conditions necessary to perform diverse operations on typical functional groups.

Pyrazabole is stable to aqueous alkali but is degraded to boric acid and pyrazole when refluxed in hydrochloric acid. 4,4,8,8-Tetraethylpyrazabole behaves similarly. However, both survive contact with dilute acid at room temperature. The stability toward acid is increased markedly by appropriate substitutions. Thus 4,4,8,8-tetraethyl-2,6-pyrazaboledicarbonitrile (IXa) was recovered unchanged after 24-hr reflux in constant-boiling hydrochloric acid as was 2,6-pyrazaboledicarbonitrile. On the other hand IXa, when refluxed in aquo-alcoholic alkali and then acidified, yielded the corre-



IXa, R = CN
b, R = COOH
c, R = COONa
d, R = Br
e, R = Li
f, R = CHO
g, R = NO_2
h, R = NH_2
i, R = $N(COCH_3)_2$

sponding 2,6-dicarboxylic acid, IXb, in 90% yield. A disodium salt IXc was obtained from IXb by titration. The integrity of the pyrazabole ring in this and subsequent examples is proved best by proton nmr spectra which confirm the equivalence of the 1,3,5,7 hydrogens in the products and thus the intactness of the pyrazabole ring. The enhanced stability to acid of –CN substituted pyrazabole may be ascribed to two factors: the inductive effect of the cyano group which removes electrons from the ring nitrogen atoms, the expected sites of protonation during acid hydrolysis; and the availability of an alternative protonation target, the nitrile nitrogen, which would render the BN bond immune to further protonation. The 2,6-dibromo-4,4,8,8-tetraethylpyrazabole (IXd) behaved much like a normal aromatic bromide and reacted with butyllithium to yield the 2,6-dilithio derivative, IXe. The structure of this compound was proved by carbonation and acidification which gave an acid identical with that obtained from hydrolysis of the dinitrile IXa.

The 2,6-dilithio derivative was also converted to the 2,6-dicarboxaldehyde, IXf, upon treatment with methyl formate. Structure IXf was confirmed by infrared and nmr spectra as well as by the formation of a 2,4-DNP derivative.

The 2,6-dinitro derivative, IXg, was catalytically hydrogenated to the diamino derivative, IXh, which proved to be somewhat sensitive to air. Reaction of IXh with excess boiling acetic anhydride gave the stable tetraacetyl derivative, IXi.

These examples show the pyrazabole ring to be a rather durable entity that can survive a wide range of conditions leading to diversely substituted pyrazaboles. Although pyrazaboles as a class are not as stable as some of the polyhedral boranes[8] or carboranes,[9] they compare very favorably in terms of availability, hydrolytic and oxidative stability, as well as wealth of derivative chemistry with borazoles or other boron–nitrogen heterocycles.[10]

Experimental Section

The pyrazabole starting materials were prepared as described before.[2]

4,4,8,8-Tetrachloropyrazabole. A solution of 16.0 g (0.1 mole) of pyrazabole in 800 ml of carbon tetrachloride was stirred, and chlorine was bubbled in until the yellow color persisted. Hydrogen chloride was evolved, and a white solid precipitated. The mixture was stirred for 1 hr and filtered. There was obtained 29 g (97%) of a product melting at 215–220°. It melted after recrystallization from chlorobenzene and sublimation at 222–223°.

Anal. Calcd for $C_6H_6B_3Cl_4N_4$: C, 24.2; H, 2.01; Cl, 47.7. Found: C, 24.9; H, 2.13; Cl, 47.8.

The ultraviolet spectrum showed λ_{max} 225 mμ (ε 15,100), 220 mμ (ε 15,500), and 214 mμ (ε 13,500).

4,4,8,8-Tetrabromopyrazabole. A solution of 16 g (0.1 mole) of pyrazabole in 400 ml of carbon tetrachloride was stirred at room temperature. A solution of 64 g (0.4 mole) of bromine in 100 ml of carbon tetrachloride was added dropwise. Hydrogen bromide was evolved. The hot solution was stirred overnight and filtered. The product was recrystallized from chlorobenzene and obtained in 25.0 g (52%) yield. The material sublimes *in vacuo* and melts at 291–293°.

Anal. Calcd for $C_6H_6B_2Br_4N_4$: C, 15.2; H, 1.26; Br, 67.2; N, 11.7. Found: C, 15.3; H, 1.24; Br, 66.2; N, 11.6.

The ultraviolet spectrum showed λ_{max} 226 mμ (ε 17,900).

4,4,8,8-Tetraiodopyrazabole. Iodination of pyrazabole with iodine in carbon tetrachloride gave sublimable 4,4,8,8-tetraiodopyrazabole, as judged by the absence of BH stretching in the infrared spectrum. The compound, however, decomposed on standing.

4,4,8,8-Tetrafluoropyrazabole. A mixture of 6.8 g of pyrazole and 12.7 g of trimethylamine trifluoroborane (both 0.1 mole) was stirred and refluxed in 200 ml of toluene for 24 hr. The reaction mixture was evaporated to dryness at aspirator vacuum, and the residue was stirred with 200 ml of water. The mixture was filtered, and the solid was sublimed to give 1.2 g (10%) of crystalline material, mp 170–172°, identical in all respects with the authentic compound.[3]

4,4,8,8-Tetrachloro-1,3,5,7-tetramethylpyrazabole. Chlorine was bubbled into a solution of 1,3,5,7-tetramethylpyrazabole until the yellow color persisted. The product was obtained in 82% yield and was purified by recrystallization from toluene, mp 308–309°.

Anal. Calcd for $C_{10}H_{14}B_2Cl_4N_4$: C, 33.9; H, 3.95; N, 15.8. Found: C, 33.6; H, 4.05; N, 15.5.

4,4,8,8-Tetrachloro-2,6-diisopropylpyrazabole. A mixture of 4-isopropylpyrazole[11] (5.1 g, 0.046 mole) and trimethylamine borane (3.38 g, 0.046 mole) was refluxed overnight in 40 ml of toluene. After solvent evaporation, 2,6-diisopropylpyrazabole was obtained as an oil which did not solidify even on prolonged standing and cooling.

The product was dissolved in 200 ml of carbon tetrachloride and exhaustively chlorinated by bubbling in chlorine until the yellow color persisted. The crude product was sublimed at 200° (1 mm) to give 5.3 g (60% over-all yield) of colorless solid which was purified further by recrystallization from heptane. It melts at 207–208°.

Anal. Calcd for $C_{12}H_{18}B_2Cl_4N_4$: C, 37.7; N, 4.72; Cl, 37.1. Found: C, 37.7; H, 5.10; Cl, 36.8.

2,6-Dibutyl-4,4,8,8-tetrachloro-1,3,5,7-tetramethylpyrazabole. A. 3,5-Dimethyl-4-butylpyrazole was prepared by mixing equimolar amounts of 3-butylpentane-2,4-dione[12] and hydrazine hydrate in methanol. It was purified by distillation *in vacuo*, bp 119–120° (1 mm). It solidified on standing (mp 44–45°) and was obtained in 78% yield.

Anal. Calcd for $C_9H_{16}N_2$: C, 71.0; H, 10.6; N, 18.4. Found: C, 71.1; H, 10.6; N, 18.6.

B. A mixture of 0.1 mole of 4-butyl-3,5-dimethylpyrazole and 0.11 mole of trimethylamine borane in 200 ml of benzene was refluxed overnight. The solution was stripped of solvent to yield 2,6-dibutyl-1,3,4,7-tetramethylpyrazabole as an oil that could be neither crystallized nor distilled.

The crude material was dissolved in 200 ml of CCl_4 and exhaustively chlorinated yielding 22 g (94%) of crude product. After recrystallization from toluene and then sublimation, the compound melts at 244–245°. The B^{11} nmr spectrum consists of a singlet at +16.3 ppm (referred to trimethyl borate).

Anal. Calcd for $C_{18}H_{30}B_2Cl_4N_4$: C, 46.4; H, 6.45; Cl, 30.5. Found: C, 46.9; H, 6.65; Cl, 30.2.

4,8-Dichloro-2,6-bis(perfluoroisopropyl)pyrazabole. Crude 2,6-bis(perfluoroisopropyl)pyrazabole (3.2 g) was dissolved in a 1:1 mixture of chloroform and carbon tetrachloride, and chlorine was bubbled in until the yellow color persisted. The solvents were evaporated, and the residue was recrystallized from toluene and sublimed. There was obtained 2.6 g (72%) of solid, mp 143–144°.

Anal. Calcd for $C_{12}H_6B_2Cl_2F_{14}N_4$: C, 25.5; H, 1.06; F, 47.2; Cl, 12.6. Found: C, 25.7; H, 1.33; F, 47.2; Cl, 13.6.

The infrared spectrum has a B–H singlet, in accord with a 4,8 location of the two chlorine atoms.

4,4,8,8-Bis(*o*-phenylenedioxy)pyrazabole. A. A mixture of pyrazabole (6.0 g, 0.038 mole) and pyrocatechol (8.5 g, 0.077 mole) was heated until hydrogen evolution ceased. The melt solidified on cooling. The product was recrystallized from boiling toluene yielding 8.6 g (85%) of solid, which was further purified by dissolving it in methylene chloride and extracting unreacted pyrocatechol with dilute sodium hydroxide. The methylene chloride layer was evaporated to dryness and the residue was sublimed. The pure product melts at 232–233°.

Anal. Calcd for $C_{18}H_{14}B_2N_4O_4$: C, 58.1; H, 3.76; N, 15.0. Found: C, 58.4; H, 4.04; N, 14.9.

The ultraviolet spectrum has λ_{max} 279 mμ (ε 9570) and sh 285 mμ (ε 7490). The nmr spectrum consists of a doublet (J = 2.5 cps) at τ 2.18, an A_2B_2 multiplet centered at τ 3.07, and a triplet (J = 2.5 cps) at τ 3.50 in a 2:4:1 ratio.

B. To a stirred and nitrogen-blanketed solution of 11.0 g (0.1 mole) of pyrocatechol in 150 ml of tetrahydrofuran was added 100 ml of 1.0 *M* solution of borane in tetrahydrofuran. After hydrogen evolution ceased (4.8 l.), 6.8 g (0.1 mole) of pyrazole was added, and the solution was refluxed until another 2.4 l. of hydrogen was evolved. The solution was evaporated to dryness, and the residue was recrystallized from toluene yielding 12.4 g (67%) of 4,4,8,8-bis(*o*-phenylenedioxy)pyrazabole, identical in all respects with the material from the preceding experiment.

4,4,8,8-Tetraphenoxypyrazabole. A mixture of 18.8 g of phenol (0.2 mole) and 8.0 g (0.05 mole) of pyrazabole was stirred and refluxed until about 5 l. of hydrogen was evolved. The melt solidified on cooling. The product, obtained in 26.4 g (100%) yield, was recrystallized from 2:1 heptane–toluene and melted at 183–184°.

Anal. Calcd for $C_{30}H_{26}B_2N_4O_4$: C, 68.1; H, 4.93; N, 10.6. Found: C, 67.8; H, 4.79; N, 10.8.

The nmr spectrum has a doublet (J = 2.6 cps) at τ 2.22, a multiplet around τ 3.1, and a triplet (J = 2.6 cps) at τ 3.78 in 2:10:1 ratio.

Reaction of Pyrazabole with *o*-Phenylenediamine. A mixture of 0.8 g (0.005 mole) of pyrazabole and 1.08 g (0.01 mole) of *o*-phenylenediamine was heated in a test tube with a soft Bunsen burner flame. Hydrogen was evolved; then the melt bubbled vigorously, then started to solidify. It was cooled to 150°, stirred with toluene, and filtered. The product was washed with ether to give, after air drying, 0.5 g (90% yield). It melted at 405–407° and sublimed *in vacuo*.

Anal. Calcd for $C_{18}H_{13}B_3N_6$: C, 62.2; H, 4.32. Found: C, 62.2; H, 4.39.

(8) M. F. Hawthorne in "The Chemistry of Boron and Its Compounds" E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., 1967.

(9) T. Onak, *Advan. Organometal. Chem.*, **3**, 263 (1965).

(10) K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Academic Press Inc., New York, N. Y., 1965.

(11) V. T. Klimko, T. V. Protopopova, and A. P. Skoldinov, *Zh. Obshch. Khim.*, **31**, 170 (1960).

(12) F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3635 (1950).

The same material was obtained on heating an equimolar mixture of trimethylamine borane and *o*-phenylenediamine. Both products had infrared spectra identical with authentic 5H,12H,19H-tris(1,3,2-benzodiazaborolo)borazine.[6]

Hydrolysis of 4,4,8,8-Tetraethylpyrazabole-2,6-dicarbonitrile, 4,4,8,8-Tetraethylpyrazabole-2,6-dicarboxylic Acid, and Its Sodium Salt. One gram of 4,4,8,8-tetraethylpyrazabole-2,6-dicarbonitrile (0.0033 mole) in 25 ml of 10% NaOH and 10 ml of ethanol was stirred and refluxed. The material dissolved slowly and ammonia was evolved. After 24 hr the solution was acidified with hydrochloric acid. The precipitated solid was filtered and air dried to give 1.0 g (90%) of white crystals. The product was recrystallized from aqueous ethanol. It does not melt, but slowly turns yellow at 300°, remaining solid at 400°.

Anal. Calcd for $C_{16}H_{26}B_2N_4O_4$: C, 53.4; H, 7.23. Found: C, 53.6; H, 7.46.

The nmr spectrum (in acetone-d_6) was consistent with the structure, having a singlet at τ 2.27, a broad singlet at τ 3.94, and a complex multiplet centered at τ 9.92, with relative areas 2:1:10 assigned to 1,3,5,7 hydrogens, the acid hydrogens, and the B-ethyl groups, respectively. A small sample of the diacid was titrated to phenolphthalein end point with sodium hydroxide, and the aqueous solution was diluted with acetone. A colorless crystalline solid separated. It was filtered and dried at 290° (1 mm). This salt decomposes around 420°.

Anal. Calcd for $C_{16}H_{24}B_2N_4NaO_4$: C, 47.5; H, 5.94. Found: C, 47.1; H, 6.06.

In contrast to alkaline hydrolysis was the inertness of the nitrile groups to acid. Thus, refluxing of 1 g of dinitrile in a mixture of 20 ml of 20% hydrochloric acid and 10 ml of ethanol for 24 hr resulted in complete recovery of unchanged starting material.

2,6-Dilithio-4,4,8,8-tetraethylpyrazabole and Its Carbonation. To a solution of 10.8 g (0.025 mole) of 2,6-dibromo-4,4,8,8-tetraethylpyrazabole in 300 ml of ether was added (under N_2) 35 ml of butyllithium solution (15% in hexane; d = 0.68 g/ml). A white precipitate promptly separated. The mixture was stirred and refluxed for 30 min. It was then blanketed with gaseous CO_2 until no further CO_2 was absorbed. The reaction mixture was then stirred with water and dilute hydrochloric acid. The organic layer was separated, dried with magnesium sulfate, filtered, and evaporated to dryness, yielding 7.3 g (81%) of product with an infrared spectrum identical with that of the material obtained from hydrolysis of the corresponding 2,6-dicarbonitrile.

4,4,8,8-Tetraethylpyrazabole-2,6-dicarboxaldehyde. The 2,6-dilithio derivative was prepared as in the preceding experiment. The mixture was cooled to −20° and 40 ml of methyl formate (large excess) was added all at once. The mixture was allowed to warm to room temperature. It was shaken with dilute aqueous hydrochloric acid, and the organic layer was separated, dried, filtered, and stripped of solvent. The syrupy residue solidified partially on trituration with a mixture of ether and pentane. The solid was recrystallized from heptane yielding 3.6 g (48%) of crystals, mp 124–125°.

Anal. Calcd for $C_{16}H_{26}B_2N_4O_2$: C, 58.6; H, 7.93. Found: C, 58.6; H, 7.90.

The infrared spectrum shows aldehyde bands (CH at 2750 cm^{-1} and CO at 1690 cm^{-1}). The nmr spectrum is confirmatory with singlets at τ −0.14 (CHO) and τ 1.77 (1,3,5,7 hydrogens), and a three-peak system centered at τ 9.35 with relative areas of 1:2:10.

4,4,8,8-Tetraethyl-2,6-diaminopyrazabole and Its Tetraacetyl Derivative. A Parr bottle containing 4,4,8,8-tetraethyl-2,6-dinitropyrazabole (4.5 g, 0.012 mole), 0.2 g of 5% palladium on carbon, and 200 ml of ethanol was shaken at 40 psi hydrogen pressure until hydrogen ceased to be absorbed. The mixture was filtered, and the filtrate evaporated to dryness to give 2.9 g (78%) of slightly pinkish solid. It was recrystallized from *n*-heptane and melted at 125–126°.

Anal. Calcd for $C_{14}H_{28}B_2N_6$: C, 55.7; H, 9.28; N, 27.8. Found: C, 56.4; H, 9.42; N, 28.1.

The nmr spectrum was confirmatory with a singlet at τ 2.77, a singlet at τ 6.93, and an apparent singlet at τ 9.40 with relative areas of 1:1:5.

A small sample of this compound was exhaustively acetylated by boiling briefly in acetic anhydride and cooling the solution. The tetraacetyl derivative was obtained as colorless crystals, mp 212–213°.

Anal. Calcd for $C_{18}H_{32}B_2N_6O_2$: C, 56.2; H, 7.67. Found: C, 56.1; H, 7.99.

The nmr spectrum has singlets at τ 2.40 and 7.64 and an apparent triplet at τ 9.38 in 1:3:5 ratio, in accord with the tetraactyl structure. The infrared spectrum has no NH bands.

4,4,8,8-Tetrakis(1-pyrazolyl)pyrazabole. A. From Pyrazabole and Pyrazole. A mixture of 34 g (0.21 mole) of pyrazabole and 6.0 g (0.88 mole) pyrazole was heated with stirring until the theoretical amount of hydrogen (about 22 l.) was evolved. The melt, after cooling, was recrystallized from boiling toluene. There was obtained 34 g (38%) of colorless crystals, mp 259–260°. Concentration of the filtrate yielded a second crop of 40 g (36%). The compound sublimes *in vacuo*.

Anal. Calcd for $C_{15}H_{15}B_2N_{12}$: C, 50.9; H, 4.25; B, 5.09; mol wt, 424. Found: C, 51.4; H, 4.50; B, 5.55; mol wt (ebullioscopic in benzene), 399.

The ultraviolet spectrum has λ_{max} 217 mμ (ϵ 3100). The nmr spectrum (in $CDCl_3$) consists of an unresolved set of two overlapping doublets at τ 2.3, a doublet (J = 2.4 cps further split into doublets, J = 0.5 cps) at τ 3.19, a triplet (J = 2.6 cps) at τ 3.30, and a "triplet" resolvable into two overlapping doublets (J = 2.4 and 1.7 cps) centered at τ 3.84, with relative intensities 4:2:1:2. They were assigned to overlapping 3 (or 5) pyrazole H and 1,3,5,7 pyrazabole H's, the 5 (or 3) pyrazole H, the 2,6 pyrazabole H's and the 4 pyrazole H, respectively.

B. From Boron Trichloride and Pyrazole. Boron trichloride gas was passed just above the surface of 68 g (1 mole) of molten pyrazole. The solution was kept at 100° by periodic cooling. When no further reaction seemed to be taking place, the flask contents were briefly heated to 220–225°. Vigorous ebullition took place. When it subsided, volatile materials were distilled at 150–180° (aspirator vacuum). The solidified pot residue was dissolved in water, and this solution was stirred with a large excess of 50% sodium hydroxide. A solid precipitated. It was filtered, washed with water, and recrystallized from dimethylformamide to give 5.0 g (16%) of colorless crystals, identical in all respects with the product from A.

4,8-Bis(1-pyrazolyl)pyrazabole. A mixture of 40 g (0.25 mole) of pyrazabole and 34 g (0.5 mole) of pyrazole was melted and heated ultimately at 200°, until 12.5 l. of hydrogen was evolved. The melt was cooled; it formed a syrup which, on stirring with heptane, yielded some solid. After recrystallization from toluene–heptane, it melted at 177–185°, implying a mixture of *cis,trans* isomers.

Anal. Calcd for $C_{12}H_{14}B_2N_8$: C, 49.3; H, 4.80; N, 38.3. Found: C, 49.0; H, 4.70; N, 38.3.

The nmr spectrum (in τ values) is confirmatory with doublets at τ 2.24 (J = 1.7 cps) and 2.39 (J = 2.6 cps), triplet at 3.50 (J = 2.6 cps), and a triplet-like set of overlapping doublets (J = 2.3 and 1.7 cps) centered at 3.65 in 1:3:1:1 ratio. The B^{11} nmr spectrum has a broad peak at +23.0 ppm from trimethyl borate.

4,8-Diphenylpyrazabole. A molten mixture of 0.75 g (0.005 mole) of phenylborane–trimethylamine complex and 0.34 g (0.005 mole of pyrazole was heated with a hot-air gun. Gas evolution commenced at about 90–100° and continued briskly as the melt was heated to 200°. The melt was cooled and boiled with 10 ml of heptane. A solid was obtained in 0.66 g (85%) yield. After sublimation it melted at 162–172°.

Anal. Calcd for $C_{18}H_{18}B_2N_4$: C, 69.2; H, 5.77; N, 18.0. Found: C, 69.1; H, 5.94; N, 18.2.

The nmr spectrum has a doublet (J = 2.1 cps) at τ 2.47, singlet at τ 2.76, and triplet at τ 3.68 (J = 2.1 cps) in 2:5:1 ratio. The B^{11} nmr spectrum has a very broad peak centered at +20.8 ppm from trimethyl borate.

4,8-Diphenyl-4,8-bis(1-pyrazolyl)pyrazabole. Phenylboron dichloride (28.6 g, 0.169 mole) was added to a suspension of 0.508 mole of pyrazolylpotassium in benzene, and the mixture was refluxed overnight and filtered. The solid was stirred with water again. After drying there was obtained 2.0 g of 4,8-diphenyl-4,8-(1-pyrazolyl)pyrazabole. The original benzene solution was stripped to dryness and the residue triturated with ether, yielding another 9.0 g of the same compound for a total yield of 11.0 g (14.4%). After recrystallization from dimethylformamide and sublimation the product melts at 239–240°.

Anal. Calcd for $C_{24}H_{22}N_2N_8$: C, 64.9; H, 4.96; N, 25.2. Found: C, 64.8; H, 4.89; N, 24.9.

The ultraviolet spectrum shows the aromatic fine structure at 269, 265, 263, 259, and 253 mμ (ϵ ranging from 240 to 450) and a peak at 215 mμ (ϵ 34,200). The H^1 nmr spectrum had a doublet (J = 2.5 cps) at τ 2.44, a complicated multiplet in the τ 2.7–3.3 range, a triplet at τ 3.47 (J = 2.6 cps), and a "triplet" consisting of two unresolved doublets at τ 4.12 in 6:12:2:2 ratio. They were assigned to 1,3,5,7 pyrazabole hydrogens (overlapping with 3 (or 5) pyrazole H), the phenyl group overlapping with 5 (or 3) pyrazole hydrogen, the 2,6 pyrazabole hydrogens, and the 4 pyrazole hydrogen, respectively.