CONTRIBUTION NO. 1563 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION,
E. I. DU PONT DE NEMOURS AND COMPANY, WILMINGTON, DELAWARE 19898

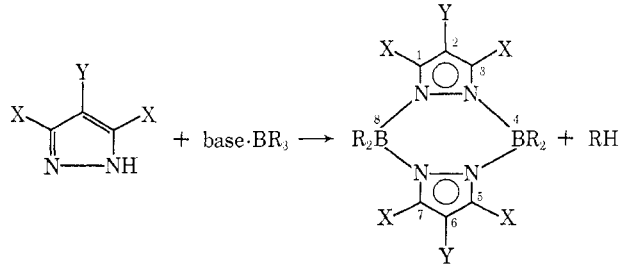
Boron–Pyrazole Chemistry. V. 4,4-Disubstituted Pyrazaboles

BY S. TROFIMENKO

Received March 20, 1969

Selectively 4,4-disubstituted pyrazaboles have been synthesized by the reaction of poly(1-pyrazolyl)borates with boranes containing at least one leaving group and particularly with dialkylboryl sulfonates. 4,4-Dialkylpyrazaboles undergo the normal reactions such as dihalogenation or formation of an *o*-phenylenedioxy derivative at the unsubstituted BH_2 group.

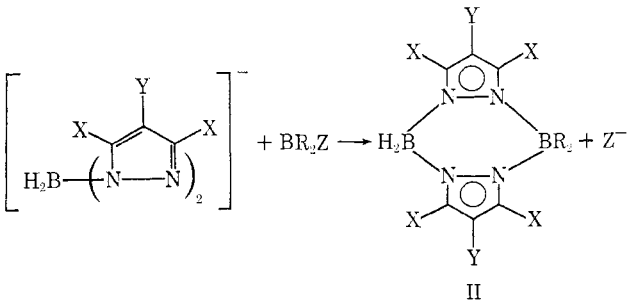
The pyrazaboles are a new class of boron–nitrogen heterocycles of remarkable oxidative and hydrolytic stability. They withstand a variety of reaction conditions used to perform operations on functional groups. Thus, by a judicious choice of pyrazole and borane components followed by other appropriate reactions it is possible to prepare a variety of pyrazaboles (I) with different substituents on carbon and boron.[1,2]



I

A necessary consequence of the above reaction path is that positions 4 and 8 bear identical substituents. While Heitsch[3] successfully prepared 4-monofluoro- and 4,4,8-trifluoropyrazaboles by fluorination of the parent compound with SF_4, a general synthetic approach to selectively 4,4-disubstituted pyrazaboles was not available, as sequential substitution on boron yields a 4,8 derivative.

In this work it was shown that selectively 4,4-disubstituted pyrazaboles can be synthesized by the reaction of a dipyrazolylborate[4,5] ion with a borane containing at least one substituent capable of being displaced as an anion



II

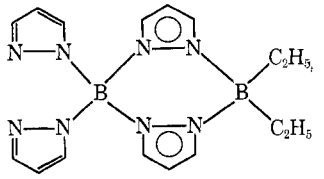
This reaction is analogous to those used to form boronium salts.[6] For instance, the reaction of $KH_2B(pz)_2$ (pz = 1-pyrazolyl) with $BF_3 \cdot O(C_2H_5)_2$ yielded II (X = Y = H, R = F) as a volatile solid, mp 87–88°. The proton nmr spectrum confirmed the asymmetric nature of substitution by the appearance of pyrazabole hydrogens as an ABC pattern, and the ^{11}B nmr spectrum indicated the presence of a BF_2 and a BH_2 grouping, respectively, by the triplets at +17.7 ppm (J = 21 cps) and at +26.5 ppm (J = 110 cps).

4,4-Dialkylpyrazaboles were synthesized by the reaction of $KH_2B(pz)_2$ with trifluoroacetoxydiethylborane or, even better, with a dialkylboryl alkane- or arenesulfonate.[7] These reagents were prepared *in situ* by the reaction of trifluoroacetic acid or the appropriate sulfonic acid with a trialkylborane. 4,4-Diethylpyrazabole was unusual in that its proton nmr spectrum indicated an A_2B system of the pyrazole ring, like a symmetrically substituted pyrazabole, and consisted of a simple doublet–triplet pattern with no additional splitting. The possibility of a 1:1 complex of pyrazabole with 4,4,8,8-tetraethylpyrazabole was ruled out since (1) the infrared spectrum was not a composite of the two suspected components and contained a new band at 820 cm^{-1}; (2) the nmr spectrum while similar to that of both symmetrical pyrazaboles differed in the chemical shift of the triplet and the distance from it, Δ, to the center of the doublet; (3) derivatives were formed by chlorination or by reaction with pyrocatechol (*vide infra*). The reason for this spectroscopic equivalence of the 1, 3, 5, and 7 positions remains obscure. This apparent equivalence is also manifested in 4,4-dibutylpyrazabole, although the 1-, 3-, 5-, and 7-hydrogens show signs of separating into two unresolved doublets. In 4,4-diethyl-1,3,5,7-tetramethylpyrazabole, on the other hand, positions 1,7 and 3,5 are distinctly different.

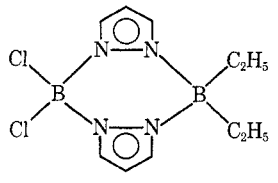
4,4-Diethyl-8,8-bis(1-pyrazolyl)pyrazabole (III) interestingly offered some insight regarding the lability of the B–N bond in pyrazaboles. If one B–N bond were easily detached to give the species $(C_2H_5)_2B(pz)B(pz)_3$, of sufficient lifetime to permit scrambling of the three uncoordinated pyrazolyl groups prior to reattachment, only one type of pyrazolyl group would be discernible by nmr. The considerations here are similar to those in

(1) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3165 (1967).
(2) S. Trofimenko, *ibid.*, **89**, 4948 (1967).
(3) C. W. Heitsch, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, No. L109.
(4) S. Trofimenko, *J. Am. Chem. Soc.*, **89**, 3170 (1967).
(5) S. Trofimenko, *ibid.*, **89**, 6288 (1967).
(6) See, for instance, H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, Chapter 11, p 458 ff.
(7) S. Trofimenko, *J. Am. Chem. Soc.*, **91**, 2139 (1969).

the case of $B(pz)_4Pd$-π-C_3H_5,[8] where the instantaneous structure involves planar, four-coordinate palladium and yet the coordinated and uncoordinated pyrazolyl groups are exchanging rapidly at room temperature, as evidenced by their nmr equivalence. Only on cooling to $-40°$ is the exchange process slowed to the



III

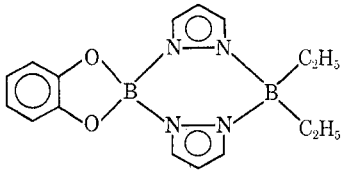


IV

point where the two coordinated pyrazolyl groups become distinguishable from the other two.

The nmr spectrum of compound III shows no indication of exchange up to $+100°$, the 8,8-pyrazolyl groups maintaining their separate identity, which is also in line with the observed stability of pyrazaboles toward nucleophiles.

The chemical reactivity of compounds II containing one BH_2 group is normal, like that of the parent pyrazabole. Thus, 4,4-diethylpyrazabole can be converted to IV by chlorination of the BH_2 group or to an *o*-phenylenedioxy derivative (V) by reaction with pyrocatechol.



V

As the above examples illustrate, the present approach, in conjunction with the direct synthesis, makes it now possible to synthesize pyrazaboles with almost any type of substitution.

Experimental Section

4,4-Difluoropyrazabole.—To a solution of 25.4 ml (0.2 mol) of $BF_3 \cdot O(C_2H_5)$ in 100 ml of ether was added slowly a solution of 18.6 g (0.1 mol) of potassium dihydrobis(1-pyrazolyl)borate in 100 ml of tetrahydrofuran. An exothermic reaction took place and solid started precipitating. When the exothermicity subsided, the reaction mixture was evaporated.

Another run on the same scale involved reverse addition. The two runs were inadvertently combined and were hence processed together by dissolving the residue from evaporation in water and extracting with methylene chloride. The extracts were evaporated yielding 29 g (75%) of an oil which solidified on standing. It was purified further by distillation *in vacuo*. The product boiled at 100° (4.7 mm), solidified, and melted, after recrystallization from hexane, at 87–88°. *Anal.* Calcd for $C_6H_8B_2F_2N_4$: C, 36.7; H, 4.08; N, 28.6. Found: C, 36.9; H, 4.68; N, 28.4.

The nmr spectrum has a doublet (J = 2.3 cps) at τ 2.09, an unresolved doublet at τ 2.35, and a poorly resolved triplet ($J \approx 2$ cps) at τ 3.61 in 1:1:1 ratio along with the BH_2 hydrogens detectable by integration in the τ 4–9 range. The infrared spectrum contains a strong BH_2 multiplet similar to that of pyrazabole.

The ^{11}B nmr spectrum has two triplets at +17.7 ppm (J = 21 cps) and +26.5 ppm (J = 110 cps) from trimethyl borate.

(8) S. Trofimenko, *J. Am. Chem. Soc.*, **91**, 588 (1969).

The ultraviolet spectrum has λ_{max} 213 mμ (ϵ 13,200).

4,4-Diethylpyrazabole. Method A.—To a solution of 30 ml (0.4 mol) of trifluoroacetic acid, stirred under nitrogen in 200 ml of benzene, was added 56.4 ml (0.4 mol) of triethylborane. Evolution of ethane commenced spontaneously and proceeded rapidly, necessitating occasional cooling. When 9.6 l. of ethane had been evolved, a solution of 75 g (0.4 mol) of potassium dihydrobis(1-pyrazolyl)borate in 400 ml of tetrahydrofuran was added slowly. An exothermic reaction took place. When it subsided, the tetrahydrofuran was distilled out and the residue was stirred with water and extracted with ether. Evaporation of the organic layer gave an oil which was distilled, the 110–140° (2.7 mm) cut being collected. It solidified on standing and was obtained in 62-g (72%) yield. The material was purified further by recrystallization from petroleum ether; mp 61–62°. *Anal.* Calcd for $C_{10}H_{18}B_2N_4$: C, 55.5; H, 8.33; N, 25.9. Found: C, 55.5; H, 8.15; N, 26.2.

The nmr spectrum consists of a doublet (J = 2.5 cps) at τ 2.43, a triplet (J = 2.5 cps) at τ 3.69, and a three-peak multiplet centered at τ 9.34, in 2:1:5 ratio. The BH_2 hydrogens can be seen by integration in the τ 3–10 range. The nmr spectrum of a 1:1 mixture of pyrazabole and 4,4,8,8-tetraethylpyrazabole is distinctly different.

The ^{11}B nmr spectrum has a broad peak at +16.5 ppm overlapping an unresolved triplet at +26.6 ppm, from trimethyl borate.

The ultraviolet spectrum has a shoulder at 215 mμ (ϵ 11,200).

Method B.—A suspension of 38 g (0.2 mol) of *p*-toluenesulfonic acid monohydrate in 250 ml of toluene was stirred and refluxed until no more water distilled into the attached Dean-Stark trap and a clear solution resulted. To this solution was added, under nitrogen, 28.2 ml (0.2 mol) of triethylborane and the solution was stirred and refluxed until 5.4 l. of gas was evolved. This solution was cooled, transferred rapidly to an addition funnel, and added dropwise to a solution of 40 g (0.2 mol) of $KH_2B(pz)_2$ in 40 ml of dry tetrahydrofuran. The mixture was refluxed briefly and was then poured into 1 l. of water. The layers were separated and the aqueous layer was extracted twice with hexane. The extracts were combined with the original organic layer, filtered, and evaporated. The residual oil was distilled *in vacuo* yielding 25 g (58%) of the main cut, bp 105–112° (3.7 mm). The infrared spectrum of the oil was identical with that of authentic 4,4-diethylpyrazabole from the preceding experiment.

4,4-Dibutylpyrazabole.—A suspension of *p*-toluenesulfonic acid monohydrate (38 g, 0.2 mol) in 250 ml of toluene was refluxed, the water being removed *via* a Dean-Stark trap. When the theoretical amount of water had been collected, the clear solution was cooled and 0.2 mol of tributylborane was added. The solution was stirred and refluxed until 0.1 mol of butane was evolved and was then cooled, transferred rapidly to an addition funnel, and added dropwise to a solution of 40 g (0.2 mol) of $KH_2B(pz)_2$ in 400 ml of THF. The mixture was refluxed briefly and was then poured into 1 l. of water. The layers were separated and the aqueous layer was extracted twice with hexane. The organic extracts were combined, dried ($MgSO_4$), filtered, and evaporated. The residue was distilled, the main cut boiling at 142–144° (1.7 mm), $n^{25}D$ 1.502. The product was obtained in 33.4-g (62%) yield. *Anal.* Calcd for $C_{14}H_{26}B_2N_4$: C, 61.7; H, 9.57; N, 20.6. Found: C, 61.7; H, 9.86; N, 20.6.

The nmr spectrum had two overlapping doublets (unresolvable) centered at τ 2.52, a triplet (J = 2.4 cps) at τ 3.83, and a complex multiplet with sharp peaks at τ 9.17 and 9.25, in 2:1:9 ratio.

The ultraviolet spectrum has λ_{max} 215 mμ (ϵ 11,900).

4,4-Diethyl-1,3,5,7-tetramethylpyrazabole.—To a mechanically stirred slurry of 29 g (0.12 mol) of potassium dihydrobis(3,5-dimethyl-1-pyrazolyl)borate in 400 ml of toluene was added slowly 100 ml of 1.2 *M* solution of diethylboryl methanesulfonate in toluene. A moderately exothermic reaction took place and the flask contents gelled partially as potassium methanesulfonate precipitated. The slurry was refluxed with stirring for 1 hr and was then cooled and stirred with 500 ml of water. The organic layer was separated, dried, filtered, and evaporated. The residue

solidified on cooling to give 26 g (96%) of solid which was purified by recrystallization from methanol; mp 91–92°. This material may also be distilled *in vacuo*, bp 158° (1.5 mm). *Anal.* Calcd for $C_{14}H_{26}B_2N_4$: C, 61.8; H, 9.56; N, 20.6. Found: C, 62.5; H, 9.22; N, 20.7.

The infrared spectrum contained the BH_2 band as a complex multiplet in the 2270–2450-cm^{-1} range.

The nmr spectrum is confirmatory: it has singlets at τ 4.14, 7.66, and 7.78 as well as a complex multiplet (B-ethyls) at τ 9.1–9.8 in the correct 1:3:3:5 ratio.

The ultraviolet spectrum has λ_{max} 219 mμ (ϵ 17,800).

4,4-Diethyl-8,8-bis(1-pyrazolyl)pyrazabole.—To a mechanically stirred slurry of 16 g (0.05 mol) of potassium tetrakis(1-pyrazolyl)borate in 200 ml of toluene was added 42 ml of a 1.7 *M* solution of diethylboryl methanesulfonate in toluene. The slurry was stirred and refluxed for 1 hr. It was then cooled, stirred with water, and extracted with ether. The organic layer was dried, filtered, and evaporated, and the residue was chromatographed on acid-washed alumina eluting first with hexane (which removed some 4,4,8,8-tetraethylpyrazabole) and then with ether which eluted the desired product. It was obtained in 12.7-g (73%) yield and was purified further by recrystallization from heptane; mp 120–121°. *Anal.* Calcd for $C_{16}H_{22}B_2N_8$: C, 55.2; H, 6.32; N, 32.2. Found: C, 55.3; H, 6.45; N, 32.8.

The nmr spectrum is confirmatory: it has two overlapping doublets at τ 2.26, a doublet (J = 2.6, J' = 0.7 cps) at τ 2.54, a doublet (J = 2.3, J' = 0.6 cps) at τ 3.05, a triplet (J = 2.5 cps) at τ 3.48, a "triplet" (overlapping doublets J = 2.3 and 1.7 cps) at τ 3.74, and an asymmetric "doublet" (B-ethyls) at τ 9.48 in the correct 2:1:1:1:1:5 ratio.

The ultraviolet spectrum has λ_{max} 218 mμ (ϵ 19,400).

4,4-Dichloro-8,8-diethylpyrazabole.—Chlorine was bubbled into a solution of 43.2 g (0.2 mol) of 4,4-diethylpyrazabole in 500 ml of carbon tetrachloride until the yellow color persisted. The solution was evaporated to dryness and the residue was recrystallized from hexane. The product was obtained in 51.5-g (90.5%) yield as colorless crystals, mp 90–91°. *Anal.* Calcd for $C_{10}H_{16}B_2Cl_2N_4$: C, 42.1; H, 5.62; Cl, 24.9; N, 19.7. Found: C, 41.5; H, 5.30; Cl, 24.4; N, 19.7.

The nmr spectrum has doublets at τ 1.76 (J = 2.5 cps) and τ 2.25 (J = 2.3 cps), a triplet at τ 3.37 (J = 2.4 cps), and a multiplet at about τ 9.4 in 1:1:1:5 ratio.

4,4-Diethyl-8,8-phenylenedioxypyrazabole.—A mixture of 10.8 g (0.05 mol) of 4,4-diethylpyrazabole and 5.5 g (0.05 mol) of pyrocatechol was refluxed in 150 ml of xylene. Hydrogen evolution was sluggish. The solvent was distilled out, whereupon hydrogen evolution speeded up and soon 2.4 l. was collected. The crude reaction mixture was chromatographed on alumina. Eluting with hexane gave 1.7 g of a solid which was identified as 4,4-diethylpyrazabole. Switching to ether–hexane as eluent produced a second fraction in 11.8-g yield (79% based on unrecovered 4,4-diethylpyrazabole). The material was recrystallized from heptane; mp 82–83°. *Anal.* Calcd for $C_{16}H_{20}B_2N_4O_2$: C, 59.6; H, 6.22; N, 17.4. Found: C, 59.2; H, 5.97; N, 17.6.

The nmr spectrum has two overlapping doublets at τ 2.23 (J = 2.6 cps) and τ 2.30 (J = 2.5 cps), each split further by 0.6 cps, a singlet at τ 3.12, a triplet at τ 3.56 (J = 2.55 cps), and a "triplet" at τ 9.29 in 1:1:2:1:5 ratio.

The ultraviolet spectrum has λ_{max} 287 mμ (ϵ 4300), 280 mμ (ϵ 5320), 275 mμ (ϵ 4480), and 215 (sh) mμ (ϵ 20,000).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MARYLAND, COLLEGE PARK, MARYLAND 20742

A Phosphorus-31 Nuclear Magnetic Resonance Study of Tertiary Phosphine Derivatives of Group VI Metal Carbonyls. III. Disubstituted Compounds[1-3]

BY SAMUEL O. GRIM AND DAVID A. WHEATLAND[4]

Received September 3, 1968

The preparation, infrared spectra, and phosphorus-31 nuclear magnetic resonance spectra are reported for 15 compounds of the type *cis*- and *trans*-$L_2M(CO)_4$, where M is Cr (*trans* only), Mo, or W, and L is tributylphosphine, dibutylphenylphosphine, or diphenylbutylphosphine. Phosphorus-31–tungsten-183 spin–spin couplings, which are observed in all of the tungsten compounds, are larger for the *trans* compounds than for the corresponding *cis* compounds. This is interpreted as being consistent with the π-bonding abilities of tertiary phosphines. The phosphorus chemical shift in the *trans* compound of a particular ligand is farther downfield than that for the corresponding *cis* compound.

Introduction

In the very recent past, the concept of π bonding between phosphorus (and similar ligands) and transition metals had been accepted and was utilized to explain or partially explain various phenomena. In platinum(II) chemistry, π bonding has been used to explain the *trans* effect,[5] the relative thermodynamic stabilities of *cis* and *trans* isomers,[6] the greater magnitude of platinum-195–phosphorus-31 coupling constants in *cis* relative to *trans* isomers,[7,8] and fluorine chemical shifts in fluorophenylplatinum compounds.[9] Also, the shorter phosphorus–platinum distance in *cis*-$((CH_3)_3P)_2PtCl_2$ compared to that of the *trans* isomer could be explained by π bonding, although the original investigators[10] were reluctant to do this.

(1) Research sponsored by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-782-67.

(2) Taken in part from the Ph.D. thesis of D. A. Wheatland, University of Maryland, 1967.

(3) Part II: S. O. Grim, D. A. Wheatland, and P. R. McAllister, *Inorg. Chem.*, **7**, 161 (1968).

(4) National Institutes of Health Predoctoral Fellow, 1965–1967.

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