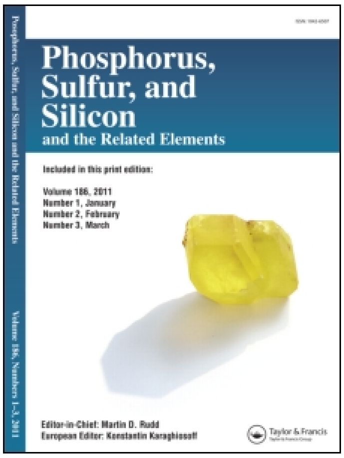

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Diethanolamines, Diphenolamines, Diethylenetriamines, the Game with Phosphorus and Boron

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DIETHANOLAMINES, DIPHENOLAMINES, DIETHYLENETRIAMINES, THE GAME WITH PHOSPHORUS AND BORON.

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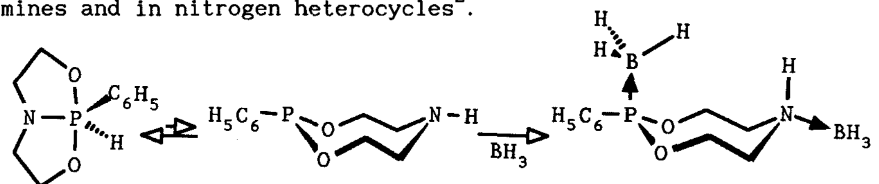
Dedicated to Prof. A. H. Cowley on occasion of his 60 birthday.

INTRODUCTION.

The nature of boron and phosphorus structures in heterocycles is determined by the ligand. We have explored the behavior of these atoms when rigid or hindered ligands are employed. The reactions produce polycyclic stable compounds in which the central atom bears uncommon functions, which in other systems, as aliphatic or unsubstituted are unstable or fleeting species. The stereochemistry and reactivity of some derivatives in which the phosphorus is the central atom of helicoidal spiranic or tricyclic structures are analyzed. We studied the dynamic and tautomeric behavior of these heterocycles using an acid or a Lewis base to shift the equilibria. In all cases comparison with the corresponding boron heterocycles is made.

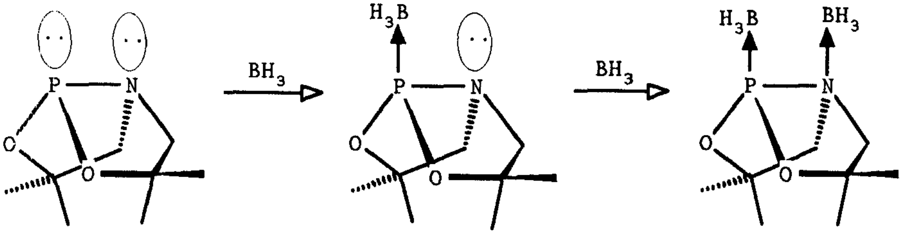
PHOSPHORUS BICYCLIC STRUCTURES AND N⇒P COORDINATION.

The first bicyclic structures of diethanolaminephosphoranes were investigated by Houalla *et al*[1]. They reported the phosphorane **1** as a very reactive compound presumably in a tautomeric equilibrium with spectroscopically undetected P(III) species. Phosphorane **1** has not basic sites owing to the retrocoordination from oxygen and nitrogen to the phosphorus atom. We were interested in evaluating its actual basic behavior and the acidic character of the P-H using BH_3. We have been currently investigating the use of borane as an steric and basic probe in amines and in nitrogen heterocycles[2].



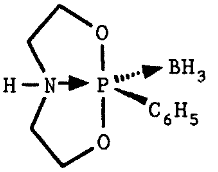
1 **2** **3**

Riess has been used BH_3 to establish the basicity order in phosphane **4** in which the addition of one equivalent of BH_3 forms the P⇒BH_3 adduct **5**[3]. The second molecule of BH_3 produced the unexpected N⇒BH_3 adduct **6**. This experiment demonstrated that owing to the geometry of **4**, phosphorus and nitrogen were tetrahedral, as a consequence the retrocoordination of N to P was hindered and the nitrogen remained as a basic sp^3 center.



4 **5** **6**

We have made to react **1** with BH_3[4]. The reaction afforded the tautomer coordinated to two BH_3 molecules **3**. The BH_3 addition probed the existence of the P(III) tautomer **2**. We attempted the synthesis of the monoadduct **7** without success. We were expecting to observe the N⇒P coordination owing to a higher Lewis acid character of the phosphorus on the presence of P-BH_3 bond as reported by Verkade for a similar compound **8**[5]. The target bicyclic **7** is an analog of the known boron heterocycle **9**[6].



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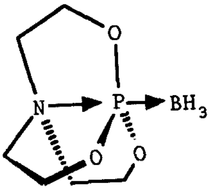

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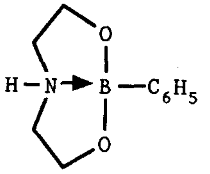
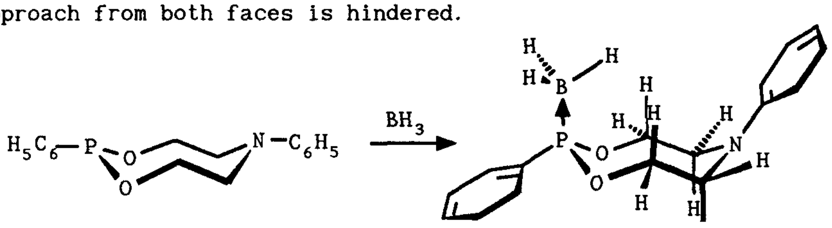


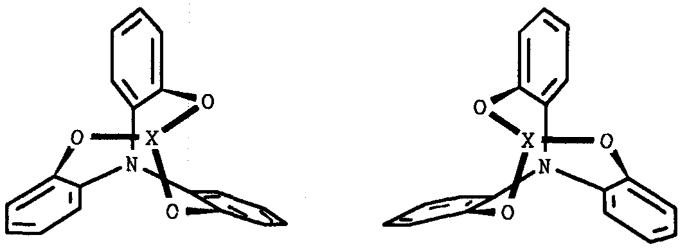
9

We have also synthesized the phosphorus eight membered heterocycle **10**[7], in which the tautomer P(V) is avoided. The reaction of **10** with an excess of BH_3-$S(CH_3)_2$ afforded **11** instead of the diadduct. This was an intriguing fact owing to that dimethylphenyl amine forms stable adducts with BH_3. We thought that a P⇒N coordination was present, but examination of the X-ray diffraction data of **11** made us reject it, in spite of the 33% TBP character of the phosphorus atom, because the P-N distance was very long (3.293 Å). Actually, the second BH_3 molecule is not coordinated because the ring is in a boat-boat conformation, and the approach from both faces is hindered.



10 **11**

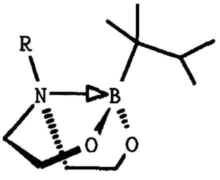
We have looked at the same phenomenon in a tricyclic aromatic structure **12**, but no evidence of a P⇒N bond was obtained. Therefore, we repeated the Verkade's experiment, making the P-BH_3 adduct. Again, the rigidity of our model was the driving force to avoid a N⇒P coordination. The corresponding boron heterocycle **13** was also prepared. Compounds **12** and **13** are pseudoatranes[8], their molecular mechanics study showed that they are helicoidal structures and therefore chiral. Now some of our future goals concerned with chiral molecules will be to obtain the crystal structures and NMR studies in alkyl substituted derivatives of these *pseudo*atranes.

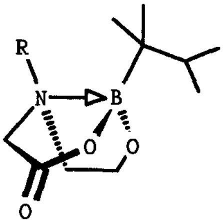


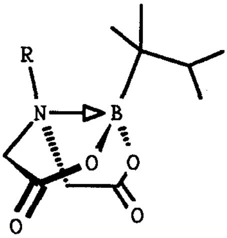
12 X = P
13 X = B

BORON BICYCLIC STRUCTURES, N⇒B COORDINATION AND CHIRAL BORON AND NITROGEN.

The study of the N⇒B coordination in bicyclic compounds and as a consequence, the preparation of optically active heterocycles in which the boron and nitrogen are chiral centers configurationally stable had been showing interesting results. We prepared several boron heterocycles and determined their N⇒B energy. We found that the N⇒B bond is a strong clasp in these compounds, even with very bulky and hindered boron atoms, a strong bond was found for ethanolamines **14**[6], and even stronger for aminoacid derivatives **15**[9] and **16**[10].





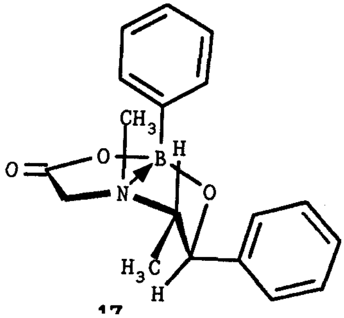


14 **15** **16**

R = H ΔG^* = 59.6 KJ > 90 KJ > 90 KJ

R = CH3 ΔG^* = 49.2 KJ

The stable boron aminoacid heterocycles were optically active compounds. From two possible isomers only one was favored in which boron and nitrogen were stable chiral centers as in compound **17**[11]. The NMR and the X-ray diffraction studies gave us the configuration of the chiral centers. We have obtained variations of the same melody with compounds **18**[12] and **19**[13].



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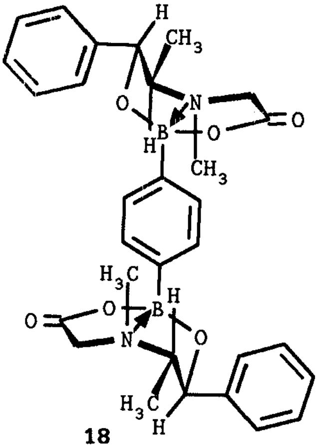

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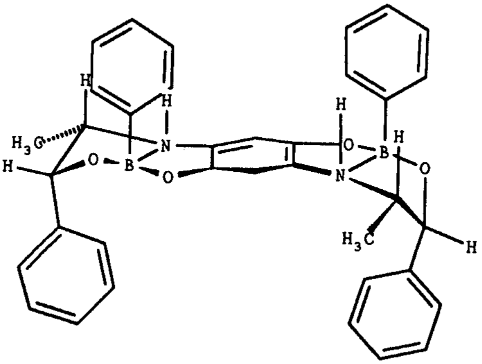
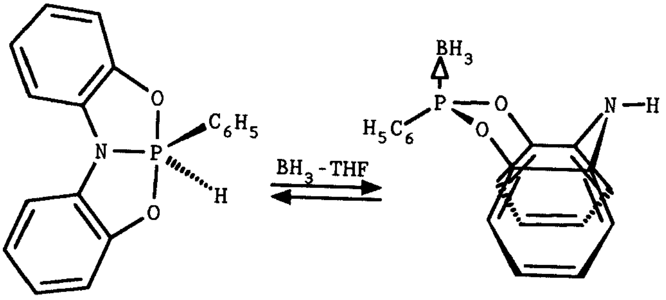


19

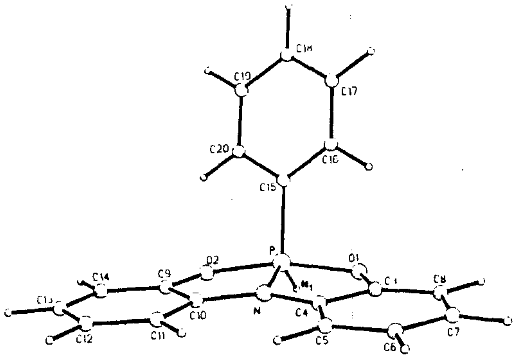
BORON AND PHOSPHORUS DIPHENOLAMINE HETEROCYCLES.

We investigated some rigid boron and phosphorus bicyclic models derived from diphenolamine. We have prepared compound **20**[14], which is more stable that the aliphatic analog[1] **1**. This phosphorane **20** is stable in water and does not exchange the P-H bond in D_2O even in presence of triethylamine or p-toluensulfonic acid[14]. Treatment with NaH followed by ICH_3 did not substitute the P-H by $P-CH_3$ as it was shown for compound **1**[1]. The reaction with BH_3-THF opened the heterocycle **20** to give the monoadduct $P \Rightarrow BH_3$ **21** (35%). Vacuum evaporation of the THF solution of **21** allow us to recover the phosphorane **20**. The X-ray diffraction study showed that the tetracyclic structure of **20** is almost planar with the phenyl group in apical position and the phosphorus in a "Berry exchange coordinate" geometry[15].



20 **21**

It was interesting to compare the structure of **20** with the corresponding boron heterocycle **22**[16], which is also stable. In **22** the boron and nitrogen are both tetrahedral, and the tetracyclic structure has an important dihedral angle (≃ 115°). We can describe **20** and **22** as *pseudo*tautomers. A proof of the unusual stability of both bicyclic systems was the fact that in the mass spectra the naked structures were found as the corresponding base peaks[16].



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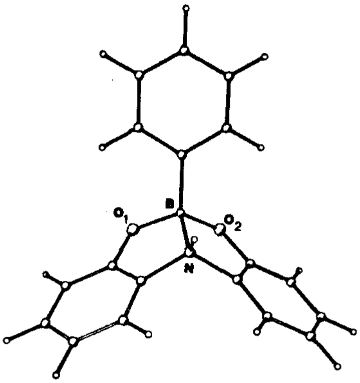
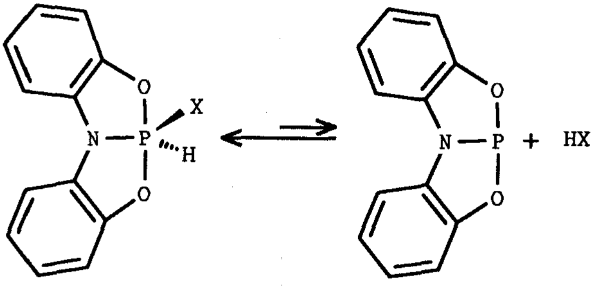


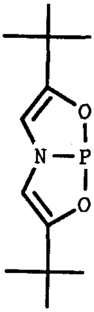
22

These rigid and stable aromatic structures inspire us in the synthesis of some phosphorus species that were reported as unstable and fleeting species in the aliphatic systems[1]. We were interested in preparing some ester **23** and amide **24** analogs to **20**[17]. Compounds **23** and **24** were very stable and they were isolated and characterized by spectroscopy. Their behavior was in contrast with that of aliphatic analogs[1].



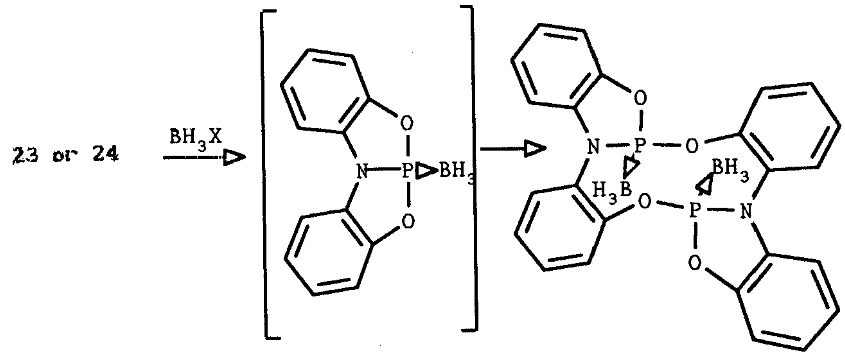
23 X = OR
24 X = NR2

25



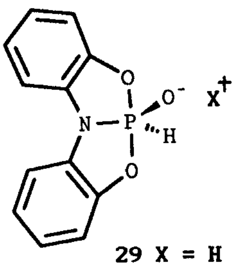
26

We have attempted to synthesize the aromatic phosphane **25** analog to the folded compound reported by Riess **4**[3] or to the planar heterocycle of prepared by Arduengo **26**[18] by elimination of an alcohol or the amide from the P(III)-P(V) equilibria **23** **25** or **24** **25** by heating the corresponding phosphoranes in vacuum. Our effort was unsuccessful because the pentacoordinated forms **23** and **24** were much more stable than the phosphane **25**[17]. We have used some borane reagents in order to make a boron derivative of the amine or the alcohol to shift the equilibrium. With BH_3 and **23** or **24** we got the dimer **28** of the phosphane ($P-BH_3$) **27**. Evidently, **27** is a very reactive compound that easily dimerizes.

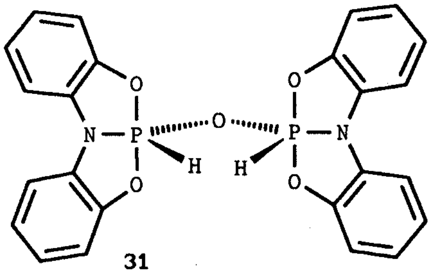


27 **28**

Diphenolamine allowed us to prepare some interesting derivatives of the phosphoranic acid[17] **29** which presents two acidic functions the OH and the PH both of which exchange the hydrogen atom in the presence of D_2O. By hydrolysis of the amide we have obtained the corresponding ammonium salt **30**. We have prepared also the anhydride **31**.

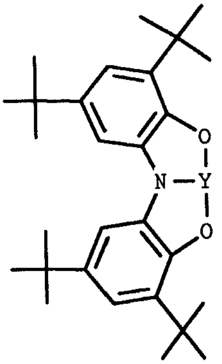


29 X = H
30 X = NH_2R_2

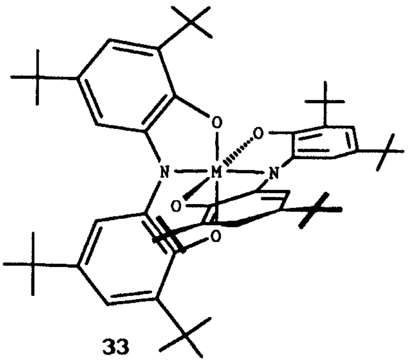


31

Recently, we have discovered the synthesis of a phosphorane **32** derived from substituted diphenolamine and two chloride functions[19,20]. Compound **32** has been prepared from reaction of PCl_3 and the metallic complex **33**, which in turn was prepared from the reaction of catechol, ammonium hydroxide and a metallic salt[21].



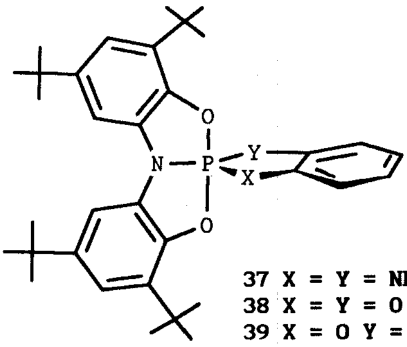
32 Y = PCl_2
34 Y = PR_2
35 Y = $P(OR)_2$
36 Y = $P(NR_2)_2$
41 Y = P
42 Y = B



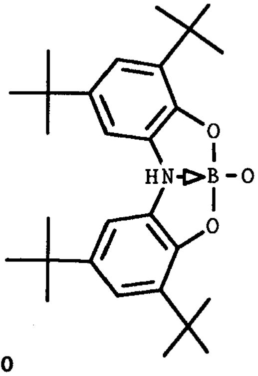
33

M= metal atom

Phosphorane **32** reacts with organolithium compounds to give the corresponding dialkyl derivatives **34**, in the presence of alcohol or amine affords the ester **35** or amide **36** respectively[19,20]. Pentacyclic compounds can be prepared by reaction with phenylenediamine **37**, catechol **38** or phenolamine **40**[20]. The reaction of **33** with BCl3 afforded a boron heterocycle whose structure is that of a N⇒B coordinated borate **40**[20]. We are now working in the preparation of the naked boron and phosphorus heterocycles **41** and **42**.



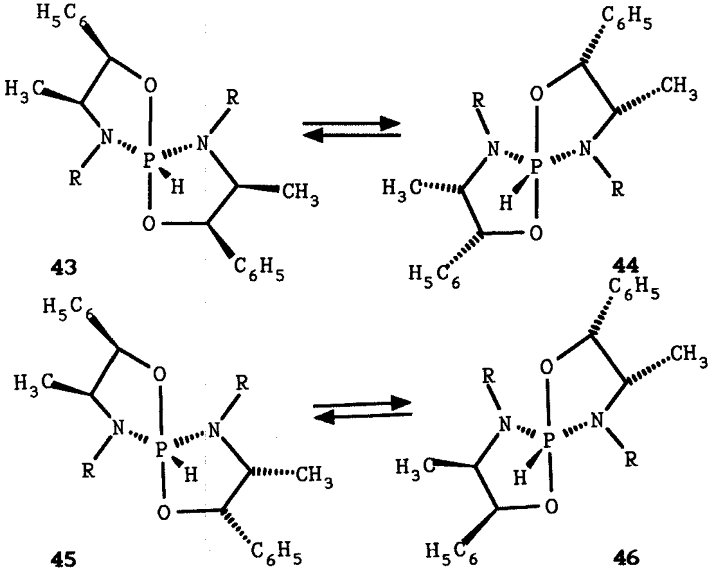
37 X = Y = NH
38 X = Y = O
39 X = O Y = NH



40

HELICOIDAL PHOSPHORUS HETEROCYCLES.

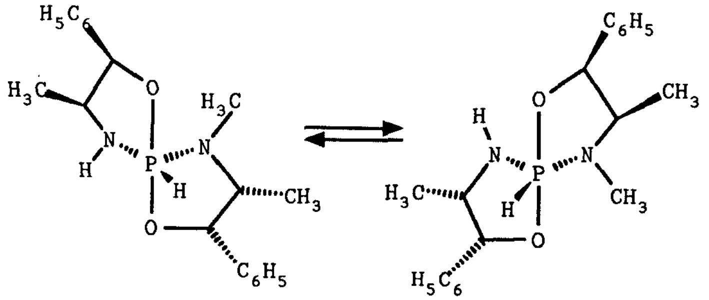
Some time ago, we have published the syntheses of phosphorane spiranic derivatives[22]. The use of optically active ligands allowed us to isolate only one isomer from twenty. The isomers of the ephedrine family gave us chiral phosphorus compounds in which the configuration of the phosphorus is relatively stable. Another interesting peculiarity of this family of compounds are the helicoidal chiral structures. The synthesis of couples of diasteromers: **43-44**, enantiomers: **45-46** or *pseudo*enantiomers: **47-48** could be possible just by choosing the correct combination of ligands.



43 **44**

45 **46**

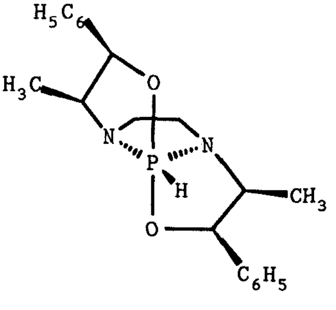
Some other phenomena added interest to this study. Each couple wa found to be in equilibrium through a Berry *pseudo*rotation. The slo crystallization afforded for the diastereomeric mixtures 100 % o transformation to only one isomer by a second order asymmetri separation. Dissolution of this crystalline isomer reverts to th initial equilibrium by a similar phenomenon to sugar mutarotation. Th phosphoranes in enantiomeric mixtures (**45-46**) have in the sam molecule two ligands in an enantiomeric relationship. It wa interesting to resolve the mixture and to examine the rotation whos value could be only the contribution of the helicoidal phosphoru atom. Resolution was not possible but fortunately the synthesis o pseudoenantiomeric (diasteromeric) couples **47-48** allowed us t crystallize only one helix **47** and to obtain its rotation[22].



$[\alpha]^{30}_{578}$ = -47.9 **47**

48 $[\alpha]^{30}_{578}$ = +48.8

Now, we are preparing tricyclic structures using the 1,2-ethylen bis(ephedrine) ligands[23]. The synthesis was completely stereo- selective to give only one isomer: **49** from two (**49** and **50**). Th tricyclic phosphorane not seen **50** has a strong steric effect from th ethylene and the substituents in the *endo* dihedral angle.



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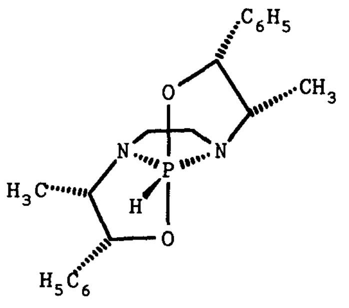
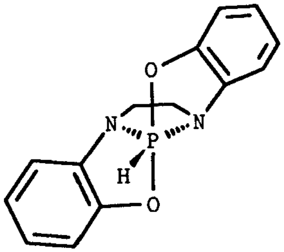


50

The tetrahedral character of the nitrogen atoms in the tricycli derivatives was evident in the phosphoranes derived fro diphenolethylenediamine. The reaction afforded two helicoida enantiomers **51**, **52**, with a C2 axis that makes the nitrogen atom equivalent[24]. Addition of BH3 demonstrated that the nitrogen atoms ar basic because a stable mono N⇒BH3 phosphorane **53** was obtained togethe with its enantiomer. Borane addition breaks the symmetry, the C2 i lost.



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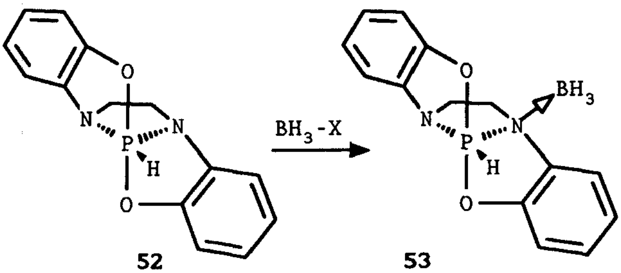
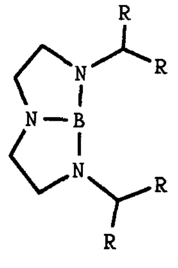


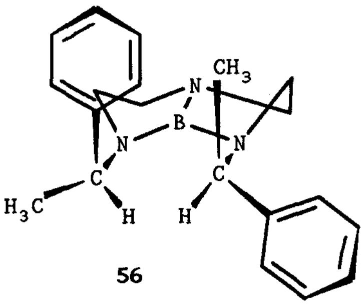
52 **53**

DIETHYLENETRIAMINE BORON HETEROCYCLES

Recently, we have been interested in the synthesis of tricoordinated boron in a bridge position of a bicyclic-octane molecule **54-55**. The previous attempts were not successful[25] because this kind of molecules are reactive and dimerizes very easily[26]. Heterocycles **54-55** were prepared with the aid of a diethylene triamine with bulky substituents. A chiral derivative **56** was also prepared[27].



54 R = CH3
55 R = C6H5



56

CONCLUSION.

Our continued efforts to understand the structural and conformational properties of these heterocycles molecules led us to explore the rules of the games in boron and phosphorus chemistry.

ACKNOWLEDGEMENT.

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