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SURPRISING ABSENCE OF REACTIVITY TOWARDS BORANE OF A CYCLIC PHENYLAMINE IN TWO HETEROCYCLES 1,3-DIOXA-2-PHOSPHA^{III}-6-AZA-2-R-6-PHENYLOCTANE

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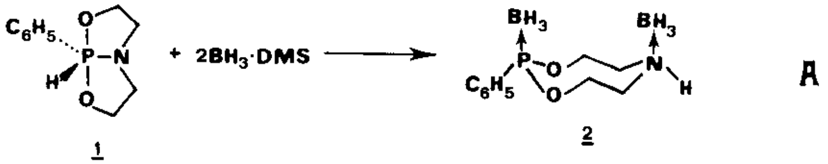
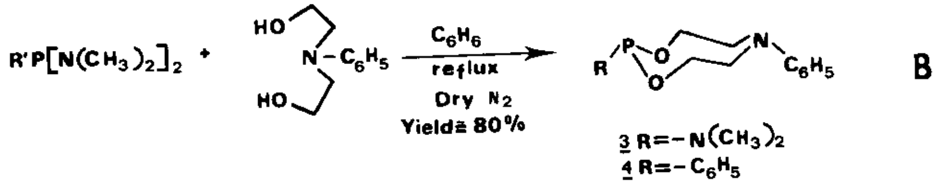
Abstract.- The title compound was reacted with an excess of $BH_3.SMe_2$ and only one BH_3 molecule was added. This phenomenon is discussed.

In a recent article[1], we have reported the reaction of BH_3.DMS with a bicyclic phosphorane 1 by the reaction A. A compound of structure 2 was isolated from the reaction. Addition of only one equivalent of BH_3.DMS to 1 gave a mixture of 1 and 2.



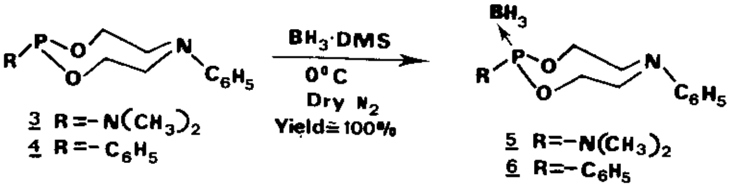
Trying to synthesize some diadducts of similar structure we have prepared compounds 3 and 4. The synthesis of the new compounds 3 and 4 was done according to reaction B and a crystalline compound was obtained in each case.



3: ^{1}H NMR (C_6D_6) δ 2.60 (d, 6H, $^3J_{H-P}$= 10.5 Hz); δ 2.36-4.36 (m, 8H); δ 6.36-7.4 ppm (m, 5H). ^{31}P NMR (C_6D_6) (H decoupled) δ +153 ppm. Mass spectrum: M^+= 254 (12.9); 211 (10.6); 210 (100); 145 (5.9). IR ($CHCl_3$) ν_{POC}1054; ν_{PN}972 cm^{-1}. Mp 94°C.

4: ^{1}H NMR (DMSO) δ 3.2-3.7 (m, 4H); 3.8-4.4 (m, 4H) 6.6-6.8 (m, 3H); 7.0-7.35 (m, 2H) 7.36-7.7 (m, 5H). ^{31}P NMR (C_2H_6SO) δ +171.9 ppm. Mass spectrum: M^+= 287 (35); 146.2 (62.4); 145.2 (100); 105.1 (52.6); 104.1 (55.6). IR (KBr) ν_{POC}1050 cm^{-1}. Mp 105-107°C.

Compounds 3 and 4 react with one mole of BH_3.DMS according to the reaction C. Each reaction gave one microcrystalline stable compound. ^{11}B NMR shows that the structures correspond to the mono-adducts 5 and 6, respectively. The addition of a second molecule of BH_3.DMS did not give the diadducts even in a strong excess of BH_3.DMS.



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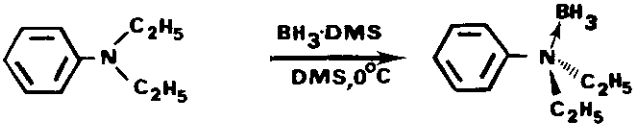
5: ^1H NMR (C_6D_6) δ 2.46 (d, 6H, $^3J_{H-P}$= 10.5); δ 2.26-4.43 (m, 8H); δ 6.2-7.3 (m, 5H); ^{31}P NMR (C_6D_6) δ 120.2 (H decoupled) (q, $^1J_{P-B}$= 95 Hz). ^{11}B NMR (C_6D_6) δ 44.1 (H decoupled) (d $^1J_{B-P}$= 96 Hz). Mass spectrum: M^+= 268 (12); 267 (15); 211 (14); 210 (100). IR ($CHCl_3$) ν_{B-H}2400, ν_{POC}1040 ν_{P-N}993 cm^{-1}. Mp 115°C.

6: ^1H NMR (C_2D_6SO) δ 3.4-4.6 (m, 8H); δ 6.6-6.85 (m, 3H); δ 7.1-7.35 (m, 2H); δ 7.35-7.9 (m, 5H) ^{31}P NMR (C_2H_6SO) δ +133 ppm. ^{11}B NMR (C_2H_6SO) δ -42 quintet. Mass spectrum: M^+ = 301 (45); 300.1 (64.1); 146.1 (89.7); 145.2 (100); 144.1 (53.4). IR (KBr) ν_{BH}2340, 2400, 2420, ν_{POC}1050 ν_{P-N}780 cm^{-1}. Mp 142°C.

DISCUSSION

Two points merit comment.

1. In compounds 3 and 5 the dimethylamino group directly bonded to phosphorus does not present any basic properties towards BH_3. This is easily explained as the effect of a back coordination π(p→d) N-P.[2]
2. The anilinic cyclic nitrogen does not react with the BH_3 contrary to what happens in compound 2. This absence of reactivity is also anomalous compared to a model compound: diethylaniline reacts quantitatively in similar conditions.[3]



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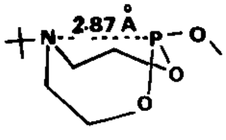
The adduct 7 presents the following spectral characteristics ^{11}B NMR (THF) δ -11.8 (q, $^{2}J_{B-H}$= 98 Hz) ^{1}H NMR ($CDCl_3$) δ -1.1 (t, J_{H-H} 9 Hz, 6H); 3.3 (q, J_{H-H} 9 Hz, 4H); 7.2-7.8 (m, 5H). IR(KBr) ν_{B-H}2296, 2359, 2411, ν_{B-N}1175, 1038 cm^{-1}.

It has been shown by X-ray diffraction analysis that the stable conformation of a cyclic phosphite 8 analogous to 3 and 4 is a boat/boat and that the P-N transannular distance is 2.87 Å in spite of the electrostatic repulsion between electronic pairs.[4,5] This important phenomenon (the interaction N-P) was cited in the literature in the study of hydrolysis of 2-oxo-2-(p-nitrophenoxy)-1,3-dioxa-2-phospha-6-methyl-6-azacyclooctane[6].



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It is possible to assume that the 5 and 6 have the same conformation as 8. This was confirmed by observation of Dreiding models which show that the least hindered conformation brings together the nitrogen and the phosphorus.

The above results indicate that the absence of reactivity of the cyclic anilinic nitrogen atom can be attributed to:

a) Steric hindrance of the nitrogen by the P-BH_3 group.

b) A bonding transannular interaction between nitrogen and phosphorus, facilitated by BH_3 coordination, that decreases the electronic density at phosphorus. Transannular interaction could not be detected by ^{31}P NMR, since compound 6 has the same δ as 2 (+133 and +132 ppm, respectively). In order to clarify this point an X-Ray study will be undertaken.

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