

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

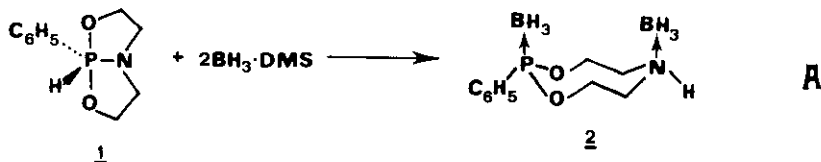
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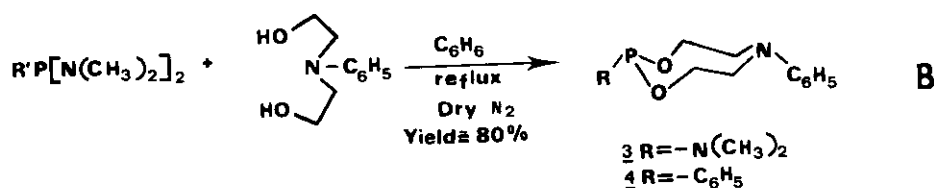
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Abstract.- The title compound was reacted with an excess of $\text{BH}_3 \cdot \text{SMe}_2$ and only one BH_3 molecule was added. This phenomenon is discussed.

In a recent article¹, we have reported the reaction of $\text{BH}_3 \cdot \text{DMS}$ 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 $\text{BH}_3 \cdot \text{DMS}$ 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.

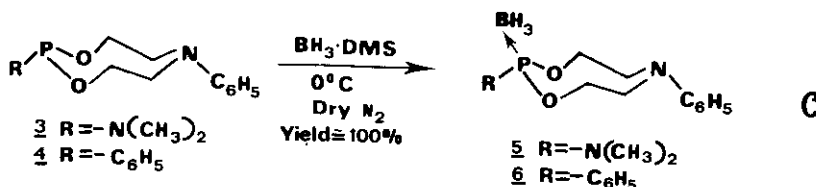


3: ¹H NMR (C₆D₆) δ 2.60 (d, 6H, ³J_{H-P} = 10.5 Hz); δ 2.36-4.36 (m, 8H); δ 6.36-7.4 ppm (m, 5H).

³¹P NMR (C₆D₆) (H decoupled) δ +153 ppm. Mass spectrum: M⁺ = 254 (12.9); 211 (10.6); 210 (100); 145 (5.9). IR (CHCl₃) ν_{POC} 1054; ν_{PN} 972 cm⁻¹. Mp 94°C.

4: ¹H 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). ³¹P NMR (C₂H₆SO) 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 $\text{BH}_3 \cdot \text{DMS}$ 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 $\text{BH}_3 \cdot \text{DMS}$ did not give the diadducts even in a strong excess of $\text{BH}_3 \cdot \text{DMS}$.



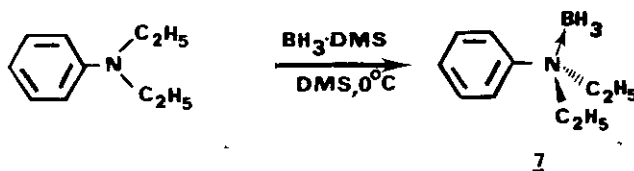
5: ^1H NMR (C_6D_6) δ 2.46 (d, 6H, $^3J_{\text{H-P}} = 10.5$); δ 2.26-4.43 (m, 8H); δ 6.2-7.3 (m, 5H); ^{31}P NMR (C_6D_6) δ 120.2 (H decoupled) (q, $^1J_{\text{P-B}} = 95$ Hz). ^{11}B NMR (C_6D_6) δ 44.1 (H decoupled) (d $^1J_{\text{B-P}} = 96$ Hz). Mass spectrum: M^+ = 268 (12); 267 (15); 211 (14);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

6: ^1H NMR ($\text{C}_2\text{D}_6\text{SO}$) 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 ($\text{C}_2\text{H}_6\text{SO}$) δ +133 ppm. ^{11}B NMR ($\text{C}_2\text{H}_6\text{SO}$) 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 $\nu_{\text{P-N}}$ 780 cm^{-1} . Mp 142°C.

DISCUSSION

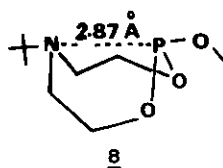
Two points merit comment.

- 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 $\pi(\text{p} \rightarrow \text{d})$ N-P.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



The adduct 7 presents the following spectral characteristics ^{11}B NMR (THF) δ -11.8 (q, $^2J_{\text{B-H}} = 98$ Hz) ^1H NMR (CDCl_3) δ -1.1 (t, $J_{\text{H-H}} 9$ Hz, 6H); 3.3 (q, $J_{\text{H-H}} 9$ Hz, 4H); 7.2-7.8 (m, 5H). IR(KBr) $\nu_{\text{B-H}}$ 2296, 2359, 2411, $\nu_{\text{B-N}}$ 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-nitro-phenoxy)-1,3-dioxo-2-phospha-6-methyl-6-azacyclooctane⁶.



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.

ACKNOWLEDGMENT

One of us (A.M.) thanks Avon Co. for a scholarship. A.K. is grateful to Conacyt Mexico for financial support. The authors thank L. Velasco and H. Bojórquez from the Instituto de Química de la Universidad Autónoma de México for Mass Spectra.

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Received, 18th March, 1983