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INTERACTION OF DIHYDROXYMETHYLPHENYLPHOSPHINE WITH THE

ISOBUTYL ESTER OF DIPHENYLBORIC ACID IN PRESENCE OF NITRILES

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While studying the reaction between dihydroxymethylphenylphosphine and the isobutyl ester of diphenylboric acid, we have previously [1] isolated 2,2,5-triphenyl-5-hydroxymethyl-2boronate-1,3-dioxane (II), instead of the expected diphenylboryloxymethyl(hydroxymethyl)phenylphosphine (I). The addition of paraform increased the yield of (II). It might seen that the reaction takes place in two stages: initially (I) is formed and then formaldehyde (FA), which originates from hydroxymethyl radicals, is added to the P-C-O-B system, and thus it would be interesting to find the conditions required for separating these stages, and to introduce other reagents capable of adding to the P-C-O-B system into the second stage. We chose as such reagents nitriles.

UDC 542.91:547.1'118:547.1'127

The reaction was studied by ³¹P NMR spectroscopy. The spectrum of the dihydroxymethylphenylphosphine, FA, and isobutyl ester of diphenylboric acid reaction mixture, containing a small excess of FA, after it had been stirred for several hours at $\sim 20^{\circ}$ C, showed no diol signal (-22 ppm) but had a signal at δ -40 ppm. As the latter signal decreased, a signal at δ 4 ppm appeared, corresponding to (II). The reaction rate depended on the temperature and the amount of FA added. However, we were unable to determine the content of the latter, since dihydroxymethylphenylphosphine dissociates to form FA.

The appearance in ³¹P NMR spectra of the reaction mixture of a signal at δ -40 ppm, which then disappears, suggests that dihydroxymethylphenylphosphine and the isobutyl ester of diphenylboric acid react by forming an intermediate product. Its signal does not split when the uncoupler is removed and has a chemical shift close to the signal produced by the sodium methylate-(I) addition product (-35 ppm), obtained from (II) in [1]. Hence the intermediate product has the structure (I).

Since (I) proved to be stable, nitriles were added to the reaction mixture with the signal δ -40 ppm. This resulted in the formation of products with δ -28 ppm and an mp of

R	CH2					Ph, NH, Me				
	^{zJ} AX	₅J _{BX}	-2JAB	δ _A	δ_{B}	δ_{Ph}	$\delta_{\rm NH}$	$_{^{3J}\mathrm{PH}}$	δ _R	Solvent
Ме	7,9 9,5	26,4 14,5	13 12	4,57 4,24	4,84 4,50	7,06-7,86	10,66	8,0	1,41	C ₆ H ₆ CH₃CN
Ph	2,3 5,7	24,6 19,3	13 13	4,74 4,44	$5,32 \\ 4,56$	7,10-7,85	9,82 10,90		7,10-7,85	C ₆ H ₆ CH ₃ CN

TABLE 1. Parameters of the PMR Spectra of (III) and (IV) (δ , ppm, J, Hz)

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 676-679, March, 1982. Original article submitted June 25, 1981. 168° in the case of acetonitrile, and with δ -30 ppm and an mp of 121° in the case of benzonitrile



R=Me (III), Ph (IV).

The compounds obtained could have an open structure, a cyclic structure with an $N \rightarrow B$ coordination bond as shown in the scheme, or a cyclic structure with a B—N bond and a proton at the P, N, and B atoms. Moreover we cannot exclude completely an open structure with a B—N bond and a hydroxymethyl group. The element composition corresponds to all the above-listed structures. The molecular weight of (IV), as determined cryoscopically in benzene, was 424 (the theoretical value is 417), thus excluding the dimeric structures (III) to (IV).

The PMR spectra of (III) and (IV) (Table 1) show the presence of protons corresponding to functional groups. The assignation of integrated intensities for the proton at the heteroatom and the methylene protons of (III) and (IV), and the methyl and methylene protons of (III) is, respectively, 1:2 and 3:2. The methylene protons are nonequivalent and have different interaction constants with the P atom nucleus. Their spectrum is typical for the system ABX, where A is axial, B is an equatorial proton, and X is the P atom nucleus. Ph occupies the equatorial, and a lone electron pair the axial position [2]. This favors a cyclic structure. The spectral parameters depend on the nature of the solvent.

In the mass spectrum of (III), a peak at 345 corresponds to a molecular ion, which together with its deutero-ion, obtained by an exchange reaction with D20 in an overlapping system at 50°, decays according to the following scheme:



An analysis of the structure of ion fragments shows that in the (III) molecule the atoms H and B are bound respectively with the atoms N and O. This corresponds to an open structure or to a cyclic structure with an $N \rightarrow B$ coordination bond.

We should bear in mind that under the given conditions (150°) products from the thermal disintegration of (III), which proceeds by the cleavage of FA, acetonitrile, benzene, or diphenylboric acid, may be superimposed on the mass spectrum of (III)



In fact the mass spectrum has ion peaks of variable multiplicity at 315, 304, 267, and 163, and also those corresponding to the molecular mass of FA, acetonitrile, benzene, and diphenyl-boric acid, which may arise from the breakdown of (III) according to the above scheme.

On the basis of PMR and mass spectral data we concluded that the compounds analyzed have a structure with strong N—H and B—O bonds and an N \rightarrow B coordination bond. The cleavage of the B—O bond and the formation of the B—N bond can apparently only occur under drastic conditions. The IR and ³¹P NMR spectra also favor such a structure. IR spectra taken of (III) and (IV) in oil have bands at 3090 and 3220 cm⁻¹, respectively. In benzene (III) absorbs at 3200 cm⁻¹. The N—H absorption region for protonated and nonprotonated imino nitrogen differ sharply (1800 to 2100 and 3100 to 3300 cm⁻¹ [3]). The signals of (III) and (IV) in ³¹P NMR spectra do not split when the uncoupler is removed.

The open structure of (III), (IV) can be considered as a substitution product in which the hydroxymethyl group in (I) is replaced by an imidoyl group. Thus, if (III) and (IV) have such a structure, an analogous reaction must take place between dihydroxymethylphenylphosphine and nitriles. However, no product formed when dihydroxymethylphenylphosphine was heated in acetonitrile. This favors the cyclic structure with a $B \rightarrow N$ coordination bond and suggests that the B atom participates in the reaction.

Hydroxymethyl derivatives of phosphine and primary phosphines react with electrophilic reagents. Products are formed with alkyl halides, acrylic acid derivatives, α -oxides, divinyl ketones, and aldehydes [4-6], by the cleavage of FA and the neutralization of the anionic electrophile center with a proton. Like the proton, the electron-deficient B atom may neutralize the anionic center. In (I), two neutralization pathways are in competition. The formation of (II) and especially (III), (IV) reveals a greater tendency for the B atom to neutralize the anionic center, which thus leads to the addition of the electrophilic reagent to the P-C-O-B system.

EXPERIMENTAL

³¹P NMR spectra were recorded on an NMR-KGU-4 spectrometer at a frequency of 10.2 MHz with proton noise suppression at a frequency of 24.3 MHz, without suppressing the 85% H₃PO₄; PMR spectra were recorded on a Varian T-60 spectrometer at 34.5°; IR spectra were recorded on a UR-10 spectrometer at $\sim 20^{\circ}$. Mass spectra were recorded at an electron-ionizing energy of 50 eV; the substances were introduced directly into the ion source, which was at a temperature of 150°.

Interaction of Dihydroxymethylphenylphosphine with the Isobutyl Ester of Diphenylboric Acid in the Presence of Acetonitrile. To dihydroxymethylphenylphosphine (4.3 g) (0.025 mole) [7] we added the isobutyl ester of diphenylboric acid (6 g) (0.025 mole), and after several minutes, CH_3CN (6 ml). The next day we filtered off the precipitate and crystallized it from CH_3CN . The yield of diphenylboryloxymethyl(acetimidoyl)phenylphosphine (III) was 7.3 g (84%), mp 166 to 168°, $\delta^{31}P - 28$ ppm (C_5H_5N , DMFA, DMSO, CH_3CN). Found: C 73.05; H 6.09; P 9.09; B 3.03; N 3.53%. $C_{21}H_{21}PNOB$. Calculated: C 73.04; H 6.09; P 8.99; B 3.19; N 4.06%. IR spectrum (ν , cm⁻¹): 3090 (oil), 3200 (C_6H_6). Mass spectrum: 346 (0.7), 345 (1.1), 344 (0.5), 315 (0-1.4), 314 (0-1.0), 304 (0.3-0.5), 303 (1.2), 302 (0.4), 269 (3.2), 268 (8.0), 267 (5.4), 183 (6.0), 182 (17), 181 (7.2), 165 (14), 164 (7.0), 163 (7.0), 152 (4.8), 151 (7.9), 123 (4.5), 122 (4.6), 110 (14.2), 109 (10), 108 (19), 107 (12), 105 (30), 104 (13), 91 (12), 79 (18), 78 (100), 77 (30), 57 (7.4), 56 (5.2), 55 (8.4), 52 (15), 51 (36), 50 (13), 42 (35), 41 (28), 30 (21).

Interaction of Dihydroxymethylphenylphosphine with the Isobutyl Ester of Diphenylboric Acid in the Presence of Benzonitrile. To dihydroxymethylphenylphosphine (9.0 g) (0.053 mole) [7], we added the isobutyl ester of diphenylboric acid (12.6 g) (0.053 mole) and benzonitrile (7 ml). The next day we filtered off the precipitate and crystallized it from CH_3CN . The yield of 2,2,5-triphenyl-5-oxymethyl-2-boronate-5-phosphonium-1,3-dioxane (II) was 2.5 g (13%), mp 132°, ³¹P 4 ppm (C₅H₅N).

On leaving the filtrate to stand, a precipitate formed. This was removed and crystallized from C_6H_6 . The yield of diphenylboryloximethyl(benzimidoyl)phenylphosphine (IV) was 8.3 g (40%), mp 121 to 123°, ³¹P - 30 ppm (C_6H_6 , CH_3CN , DMFA). Found: C 76.62; H 5.62; N 3.50%. $C_{26}H_{23}PNOB$. Calculated: C 76.66; H 5.65; N 3.44%. IR spectrum (ν , cm⁻¹): 3220 (oil).

CONCLUSIONS

The interaction of dihydroxymethylphenylphosphine with the isobutyl ester of diphenylboric acid in the presence of nitriles proceeds in two stages, one of which is a reesterification reaction and the other is the addition of the nitriles to the P-C-O-B system of the reesterification product.

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