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Synthesis and Characterization of Monosubstituted Borane Adducts of Diethyl ((Dimethylamino)methyl)phosphonate

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The cyanoborane adduct of diethyl ((dimethylamino)methyl)phosphonate, $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CN$ (**1**), was N-alkylated with Et_3OBF_4 to give the nitrilium salt $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CNEtBF_4$ (**2**). Hydrolysis of **2** with water gave the corresponding carboxyborane $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CO_2H$ (**3**), and with alkali gave the carbamoyl derivative $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CONHEt$ (**4**). Reaction of the carbamoyl compound **4** with Et_3OBF_4 followed by base treatment resulted in the formation of an imino ether, $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2C(OEt)=NR$ (**5**), which on hydrolysis yielded the ester $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CO_2Et$ (**6**). Compound **6** could be obtained in higher yields by an exchange reaction between the (aminomethyl)phosphonate and $O(CH_2CH_2)_2NCH_3{\cdot}BH_2CO_2Et$. The borane adduct $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_3$ (**7**) was formed directly by reaction of the (aminomethyl)phosphonate and $BH_3{\cdot}THF$. These compounds were characterized by spectroscopic methods and elemental analysis.

Introduction

Recently there have been a number of reports on the synthesis[1] and biological importance[2] of amine–BH_2X (X = CN, C(O)NHR, C(S)NHR, COOR, COOH, etc.) adducts. Considering the interesting chemical and biological activity of amine–BH_2X compounds and because (aminomethyl)phosphonates are also known to possess interesting biological activity,[3] we initiated studies using (aminomethyl)phosphates as the amine. In view of the potential biological activity offered through a variety of modifications, we began a systematic study of the preparation and characterization of derivatives of (aminomethyl)phosphonate–borane adducts (Scheme I). The results of that study are reported in this paper.

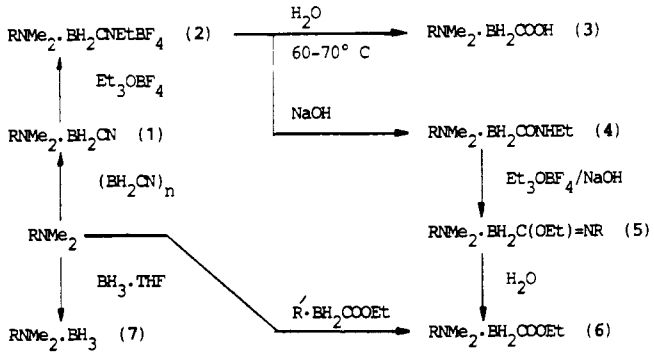
Experimental Section

Materials. The cyanoborane adduct of diethyl ((dimethylamino)-methyl)phosphate (**1**) was prepared according to a reported procedure.[4] In the preparation of the *N*-ethylnitrilium salt[1a] **2**, all glass equipment was oven-dried at 120 °C and assembled under a stream of dry nitrogen gas. An approximately 1 M solution of triethyloxonium tetrafluoroborate, prepared according to the procedure of Meerwein,[5] was used as a fresh solution.

The ^1H and ^{13}C NMR spectra were obtained on a Varian XL-300 spectrometer using TMS as an internal standard. The ^{31}P and ^{11}B NMR spectra were recorded on a JEOL FX 90Q instrument with the chemical shifts reported relative to 85% H_3PO_4 and $BF_3{\cdot}OEt_2$, respectively. The IR spectra were run on a Perkin-Elmer 1750 FT spectrometer by taking either a neat sample or a $CDCl_3$ solution of the sample between NaCl disks. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Preparation of $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CNEtBF_4$ (2). Samples of the (aminomethyl)phosphonate–cyanoborane **1** (58.5 g, 0.25 mol) and Et_3OBF_4 (500 mL, 0.5 mol) were placed in a dry flask under N_2 atmosphere and refluxed for 24 h. Dichloromethane solvent was removed at reduced pressure, and the solid residue was subjected to dynamic vacuum (0.01 mmHg) for 48 h. The light yellow solid so obtained was dissolved in a minimum amount of dry CH_2Cl_2 and cooled at 0 °C or 12 h under N_2 atmosphere to give a white solid, which was vacuum filtered under an N_2 atmosphere. Concentration of the mother liquor and cooling gave additional white solid: total yield 77 g (89%); mp 115–117 °C; hygroscopic solid.

Scheme I



$R = (EtO)_2P(O)CH_2$; $R' = O(CH_2CH_2)_2NCH_3$

Preparation of $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CO_2H$ (3). A method based on that for the amine derivatives[1b] was initially used to produce **3**. In this method, 30 mL of H_2O was stirred (3 h at room temperature) with the nitrilium salt (not purified) formed from 22.5 mL of 1 M Et_3OBF_4 in CH_2Cl_2 and 3 g (11 mmol) of the cyanoborane adduct **1**. In a second method, a 7-g (20-mmol) sample of the pure nitrilium salt **2** was dissolved in 40 mL of distilled water and heated at 60–70 °C (water bath temperature) for 5–7 min, and the reaction mixture was cooled. In both methods, the mixture was extracted with CH_2Cl_2 (4 × 30 mL) and dried over Na_2SO_4. Filtration and solvent removal gave a thick oil, which was dissolved in ether (a small amount of residue remained undissolved). If necessary, HCl(g) was bubbled into the ether solution to remove the (aminomethyl)phosphonate as its hydrochloride salt (in method 1). To the ether solution was added hexane until it gave turbidity, which on warming disappeared. The clear solution was kept at −20 °C for 24–48 h to give a white crystalline solid: Method 1, 0.81 g (25%) yield; method 2, 2.1 g (41%) yield; mp 51–53 °C. Anal. Calcd for $C_8H_{21}NBO_5P$: C, 37.93; H, 8.36; N, 5.34. Found: C, 37.73; H, 8.38; N, 5.47.

Preparation of $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CONHEt$ (4). A 17.45-g (50-mmol) sample of **2** was dissolved in 80 mL of CH_2Cl_2 and cooled in an ice bath. A cold solution of 1 N NaOH was added to attain a 13.5 pH, maintaining the temperature at −5 °C. The reaction mixture was stirred for 1 h during which time it attained ambient temperature. The organic layer was separated, and the aqueous layer was extracted two times with 40 mL of CH_2Cl_2. Combined organic extracts were dried over Na_2SO_4 and treated with activated charcoal. Filtration and solvent removal gave a white low-melting solid: yield 11.9 g (85%); mp 28–30 °C. Some preparations gave an oily product, which was purified by crystallization at −20 °C from hexanes. Anal. Calcd for $C_{10}H_{26}BN_2O_4P$: C, 42.91; H, 9.29; N, 10.00. Found: C, 42.81; H, 9.20; N, 10.03.

Preparation of $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2C(OEt)=NR$ (5). A solution of the amide **4** (3 g, 11.7 mmol) in 25 mL of CH_2Cl_2 was cooled to

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Table I. Spectroscopic (IR, ^{11}B NMR, and ^{31}P NMR) Data[a] for Borane Derivatives of Diethyl ((Dimethylamino)methyl)phosphonate

compd	IR ($CDCl_3$) ν, cm^{-1}	^{11}B NMR ($CDCl_3$) δ, ppm	^{31}P NMR ($CDCl_3$) δ, ppm
2	1250 (P=O), 2330 (C≡NEt), 2441, 2480 (B—H)	−12.95 (br, t), 0.08 (s, BF_4)	16.18
3	1250 (P=O), 1656 (C=O), 2394 (B—H), 3225 (O—H)	−7.64 (br, t)	18.71
4	1246 (P=O), 1596 (C=O), 2380 (B—H), 3349, 3435 (N—H)	−5.60 (br, t)	19.01
5	1250 (P=O), 1624 (C=N), 2375 (B—H), 3513	−7.13 (br, t)	19.01, 20.1 (3.5:1)
6	1248 (P=O), 1663 (C=O), 2400 (B—H)	−7.09 (br, t)	18.54
7	(neat) 1253 (P=O), 2374, 2320 (B—H)	−4.84 (q, J_{BH} = 93 Hz)	18.44

[a] Key: br = broad, s = singlet, t = triplet, and q = quartet.

Table II. ^1H NMR ($CDCl_3$) Spectral Data[a] for Borane Derivatives of Diethyl ((Dimethylamino)methyl)phosphonate

compd	δ, ppm (J, Hz)
2[b]	1.38 (t, J_{HCCH} = 7.1, OCH_2CH_3), 1.58 (t, J_{HCCH} = 7.4, NCH_2CH_3), 3.08 (s, NCH_3), 3.49 (d, J_{PCH} = 13.5, PCH_2), 4.22 (m, OCH_2CH_3 and NCH_2CH_3)
3	1.36 (t, J_{HCCH} = 7.1, OCH_2CH_3), 2.98 (s, NCH_3), 3.60 (d, J_{PCH} = 12.3, PCH_2), 4.17 (m, OCH_2CH_3), 9.90 (s, br, COOH)
4	1.10 (t, J_{HCCH} = 7.2, $NHCH_2CH_3$), 1.36 (t, J_{HCCH} = 7.1, OCH_2CH_3), 2.97 (s, NCH_3), 3.26 (m, $NHCH_2CH_3$), 3.85 (d, J_{PCH} = 11.7, PCH_2), 4.60 (m, OCH_2CH_3), 5.5 (s, br, NH)
5[c]	1.08 (t, J_{HCCH} = 7.4, NCH_2CH_3), 1.26 (t, J_{HCCH} = 7.1, $COCH_2CH_3$), 1.36 (t, J_{HCCH} = 7.1, $POCH_2CH_3$), 2.99 (s, NCH_3), 3.29 (q, J_{HCCH} = 7.2, NCH_2CH_3), 3.62 (d, J_{PCH} = 11.7, PCH_2), 4.02 (q, J_{HCCH} = 7.2, $COCH_2CH_3$), 4.16 (m, $POCH_2CH_3$)
6	1.24 (t, J_{HCCH} = 7.2, $COCH_2CH_3$), 1.36 (t, J_{HCCH} = 7.1, $POCH_2CH_3$), 2.98 (s, NCH_3), 3.62 (d, J_{PCH} = 12.0, PCH_2), 4.04 (q, J_{HCCH} = 7.2, $COCH_2CH_3$), 4.17 (m, $POCH_2CH_3$)
7	1.34 (t, J_{HCCH} = 7.1, OCH_2CH_3), 2.86 (s, NCH_3), 3.29 (d, J_{PCH} = 11.5, PCH_2), 4.17 (m, OCH_2CH_3)

[a] Key: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. [b] In $CDCl_3$–DMSO-d_6 solvent mixture (6:1). [c] ^1H NMR data for the major compound of the mixture.

−60 °C while keeping the flask under N_2 flow. A solution of 1 M Et_3OBF_4 (18 mL, 18 mmol) in CH_2Cl_2 was added slowly via syringe while stirring. The reaction mixture was brought to room temperature, stirred for 3 h, cooled to 0 °C and a cold solution of 1 N NaOH (50 mL) was added and stirred for 30 min. The organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 40 mL), and the combined solution of organic layers was dried over Na_2SO_4. The solvent removal at reduced pressure gave an oil to which hexane (50 mL) was added; the mixture was stirred thoroughly and kept at −20 °C overnight. The hexane solution was decanted, and the residue was washed with cold hexane. The combined fractions of hexane solution on solvent removal at reduced pressure gave a colorless thick oil, yield 2.25 g (68%). The ^{31}P NMR shows it as a mixture of two compounds approximately in 3.5:1 ratio. All attempts to separate this mixture were unsuccessful. Spectral data (Tables I–III) confirms that the major compound is **5a** (R = Et); the minor compound could not be identified due to lack of separation.

Preparation of $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_2CO_2Et$ (6). Method A. A mixture of 1.5 g of **5** and 10 mL of distilled water was placed in a round-bottom flask. The contents were warmed to 50 °C and stirred for 1 h, maintaining that temperature. The reaction mixture was then stirred at room temperature for 12 h. The solution was extracted with CH_2Cl_2 after being saturated with NaCl. The CH_2Cl_2 solution was dried over Na_2SO_4; solvent removal gave a residue, which when eluted with ether from silica gel 60 Å gave the pure ester **6**: yield 0.56 g (40%); mp 36 °C. Anal. Calcd for $C_{10}H_{25}BNO_5P$: C, 43.58; H, 8.94, N, 11.29. Found: C, 43.72; H, 8.83; N, 11.31.

Method B. A mixture of $(EtO)_2P(O)CH_2NMe_2$ (1.95 g, 10 mmol) and $O(CH_2CH_2)_2NCH_3{\cdot}BH_2CO_2Et$[6] (0.94 g, 5 mmol) was stirred at room temperature for 4 days. The reaction mixture was dissolved in ether and treated with activated charcoal. Solvent removal gave a colorless oil to which hexane solvent was added and stirred to give a two-layer mixture. When the mixture was cooled for 10 h at −20 °C, a solid product formed at the bottom of the mixture; excess amine in the hexane solution was removed by decantation. The white solid was washed twice with a small amount of hexane and subjected to vacuum to remove traces of solvent: yield 0.94 g (67% based on $O(CH_2CH_2)_2NCH_3{\cdot}BH_2CO_2Et$ used); mp 36–37 °C. The IR and all NMR data were identical with those for the ester obtained by method A. The mother liquor still contains the desired product along with free amine and *N*-methylmorpholine. However, no solid product could be obtained even after a longer cooling time.

Preparation of $(EtO)_2P(O)CH_2NMe_2{\cdot}BH_3$ (7). A mixture of $(EtO)_2P(O)CH_2NMe_2$ (10 g, 51 mmol) and $BH_3{\cdot}THF$ complex (52.5 mL, 1 N solution, 52.5 mmol) was stirred at ambient temperature for 30 min. The THF solvent and excess $BH_3{\cdot}THF$ were removed at reduced pressure, and the resulting oily product was dissolved in 100 mL of hexane to give a cloudy solution, which was cooled at −20 °C for 12 h. Hygroscopic white crystals were formed, which were dried under high vacuum after decanting the hexane solvent. Yield of the pure product was 9.06 g (85%) based on $(EtO)_2P(O)CH_2NMe_2$.

Results and Discussion

Alkylation of the cyanoborane adduct **1** with Et_3OBF_4 proceeds readily to give the corresponding nitrilium salt **2** in 89% yield. There are several reports on the conversion of crude nitrilium salts of amine–cyanoborane into their corresponding carboxyboranes and carbamoylboranes.[1a–c] When the crude nitrilium salt **2** was hydrolyzed with water either at room temperature or at 60–70 °C, the yield of the carboxyborane **3** was low (10–25%). The hydrolysis of the pure nitrilium salt of tetramethylethylenediamine–cyanoborane gave high (85%) yields.[1f] In our studies, hydrolysis of the pure nitrilium salt was carried out at different reaction times and temperatures to determine conditions for maximum yield. At 60–70 °C for 5–7 min followed by extraction with CH_2Cl_2, an optimal 41% yield of the pure carboxyborane **3** was obtained after recrystallization. Longer reaction times at room temperature gave low yields. However, hydrolysis of the pure nitrilium salt at room temperature in chloroform for 4 days gives 39% yield of carboxyborane **3**. Alkaline hydrolysis of the nitrilium salt gives a fairly good yield (85%) of the carbamoyl derivative **4**.

It appears that the (aminomethyl)phosphonate–borane adducts are less stable in acidic aqueous solution than those of the simple amine–borane derivatives. For example, $Me_3N{\cdot}BH_2CO_2H$ is moderately stable in acidic aqueous solution for several days,[1a] whereas compound **3** hydrolyzes to boric acid within hours. Presumably this could be due to a weak base–boron interaction.

Table III. $^{13}C\{^1H\}$($CDCl_3$) Spectral Data[a] for Borane Derivatives of Diethyl ((Dimethylamino)methyl)phosphonate

compd	δ, ppm (J, Hz)							
	POCC	POCC	PC	NC	NCC	NCC	COCC	COCC
2[b]	15.7 (d, J_{POCC} = 6.0)	62.7 (d, J_{POC} = 6.4)	57.0 (d, J_{PC} = 150.2)	52.4 (s)	40.5 (s)	12.6 (s)		
3	16.3 (d, J_{POCC} = 7.3)	62.7 (d, J_{POC} = 7.3)	55.5 (d, J_{PC} = 147.9)	50.4 (s)				
4	16.0 (d, J_{POCC} = 6.1)	62.2 (d, J_{POC} = 6.1)	54.9 (d, J_{PC} = 141.6)	50.1 (s)	31.5 (s)	15.0 (s)		
5[c]	16.0 (d, J_{POCC} = 5.9)	62.1 (d, J_{POC} = 6.7)	56.0 (d, J_{PC} = 146.7)	50.8 (s)	42.4 (s)	16.7 (s)	57.4 (s)	14.4 (s)
6	17.7 (d, J_{POCC} = 5.5)	64.0 (d, J_{POC} = 6.0)	56.8 (d, J_{PC} = 146.1)	51.7 (s)			57.7 (s)	16.0 (s)
7	15.6 (d, J_{POCC} = 6.9)	61.7 (d, J_{POC} = 7.3)	57.6 (d, J_{PC} = 146.5)	51.1 (s)				

[a] Key: s = singlet, d = doublet. [b] In $CDCl_3$–DMSO-d_6 solvent mixture (6:1). [c] ^{13}C NMR data for the major compound of the mixture.

Similar behavior has been observed in the stability of some amine–carboxyboranes in acidic aqueous solution.[1h] This may be the reason for low yields of **3** by acidic hydrolysis compared to **4**, which is obtained in good yield by alkaline hydrolysis. Comparative reactivity also occurs with the extremely weak acid, ethanol. When the nitrilium salt **2**, dissolved in CH_2Cl_2, is treated with absolute ethanol even at low temperature (10 °C), the B–H moiety disappears (^{11}B NMR), whereas the nitrilium salts of trimethylamine–cyanoborane[2b] and pyridine–cyanoborane[1g] do not lose B–H under these conditions. If acidic species in the phosphonate moiety such as $(HO)_2P(O)$– or $(HO)(EtO)P(O)$–$CH_2NMe_2{\cdot}BH_2CO_2H$ were generated, they could be responsible for the lower hydrolytic stability and in turn the low yield. However, the ^{31}P NMR spectrum of the hydrolysis reaction mixture shows only one other peak present (~30%), that of diethyl ((dimethylamino)methyl)phosphonate, $(EtO)_2P(O)CH_2NMe_2$. No other phosphorus decomposition products were observed. (The ^{31}P NMR chemical shift values of (aminomethyl)phosphate monoester and -phosphonic acids are upfield by 7–15 ppm from phosphonate diesters.[8])

There are several methods for the preparation of esters[1d,e,2b] of amine–carboxyboranes. However, yields of the particular ester **6** by these methods are low (5–10%). In a different approach,[7] the amide **4** is allowed to react with 2 equiv of Et_3OBF_4 followed by base treatment to give the imino ether **5** in 68% yield. The ^{31}P NMR spectrum shows that it is a mixture of two compounds approximately in a 3.5:1 ratio. The proton-decoupled ^{11}B NMR spectrum shows a slightly broad singlet. The ^1H NMR spectrum indicates that the major compound is **5a** (R = Et) by exhibiting a triplet at 1.08 ppm for the NCH_2CH_3 methyl group and a quartet at 3.09 ppm for the NCH_2CH_3 methylene group along with other expected chemical shifts for this compound (Table II). Chemical shifts for the minor compound are not well separated, and only chemical shift values for the major compound are given in Table II. The IR spectrum of this mixture shows an absorption at 3513 cm^{-1} along with the expected imino group (C=N, 1624 cm^{-1}) and other functional group absorptions (Table I). The ^{31}P NMR studies of this compound mixture with the added acid **3**, amide **4**, and ester **6** show that the ^{31}P NMR peak of the minor compound is not due to any of these compounds. It is unlikely that the minor compound is due to species such as the phosphonate monoester adduct $(HO)(EtO)P(O)CH_2NMe_2{\cdot}BH_2C(OEt)$=NEt or the phosphonic acid adduct $(HO)_2P(O)CH_2NMe_2{\cdot}BH_2C$-(OEt)=NEt, since the product mixture **5** was obtained from the organic phase after workup with an alkaline wash. The ^{31}P NMR chemical shift values for such species would be expected 6–10 ppm upfield from compound **5a**. All attempts to separate this mixture were unsuccessful. However, lack of separation does not interfere with the next step and hydrolysis of the mixture **5** at neutral pH gives 39% yield of ester after purification by column chromatography. Although this method is better than other methods for the preparation of this particular ester **6**, it involves the tedious procedure of column chromatography. When an exchange reaction[1c] was carried out between $(EtO)_2P(O)CH_2NMe_2$ and $O(CH_2CH_2)_2NCH_3{\cdot}BH_2CO_2Et$ the yield significantly increased to 67%.

Characterization of these compounds is based on IR, ^{11}B NMR, ^{31}P NMR (Table I), ^1H NMR (Table II), and ^{13}C NMR (Table III) spectroscopies and elemental analysis. The IR absorption at 2330 cm^{-1} (C≡NEt) and absence of absorption at 2199 cm^{-1} in compound **2** indicate that complete conversion occurs of nitrile **1** (C≡N at 2199 cm^{-1}) to the nitrilium salt. Characteristic B–H absorptions in the region 2375–2480 cm^{-1} are observed for each compound. All the compounds exhibit P=O stretching absorptions in the region 1246–1250 cm^{-1}. Characteristic carbonyl absorptions are observed for compounds **3**, **4**, and **6**, and the imine absorption (RC=NR, 1624 cm^{-1}) is observed for compound mixture **5** (Table I). The difference between the carboxy and amide C=O absorptions is consistent with that observed for the trimethylamine adducts.[1c]

The ^{11}B NMR spectra (Table I) of all compounds show a very broad triplet except that for **2**, which shows a broad peak for BH_2 and a sharp signal for BF_4. The BH_2 absorption collapses to a sharp singlet on proton decoupling, indicating the presence of a single BH_2 moiety. The downfield shifts of these compounds compared to those for the trimethylamine adducts provide evidence that a weaker adduct results when the (aminomethyl)phosphonate is the base. The ^{31}P NMR data (Table I) also confirm the presence of these adducts, with the signals showing an upfield shift comparable in magnitude to that observed when the parent phosphonates are compared to their HCl salts.[9]

The ^1H NMR spectra (Table II) exhibit features that are consistent with those expected from the structural assignments for these compounds. In all of these compounds, the P–CH_2 group exhibits a doublet, indicating the presence of the P–C bond; chemical shift values are far downfield from the chemical shift value observed in the corresponding uncomplexed amino phosphonate, indicating electron-density decrease due to formation of the coordinative covalent bond. The methylene group of the ethoxy function (CH_3CH_2OP) exhibits a multiplet presumably due to coupling with phosphorus and the methyl group.

The ^{13}C [^1H] NMR spectra (Table III) of (aminomethyl)-phosphonate–borane derivatives **2**–**7** also support the structural assignments for these compounds. The methyl and methylene groups of the ethoxy function in the phosphonate ester give rise to doublets in the region 15.6–17.7 ppm and 61.7–64.0 ppm, respectively, due to long-range coupling with phosphorus. The methylene group directly attached to phosphorus shows a doublet in the region 54.9–57.6 ppm with a large coupling constant value (J_{P-C} = 141.6–150.2 Hz) for these compounds (**2**–**7**), further confirming the presence of the P–C bond. The ^{13}C chemical shifts for other functional groups are consistent with the proposed structures.

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