Reactive E=C [p-p]π Systems, 45[◇]

1-Aza-3,4-diphospholenes by [3 + 2] Cycloaddition of 2-(Diisopropylamino)phosphaethyne to Diazo Derivatives $R^1R^2C{=}N_2$☆

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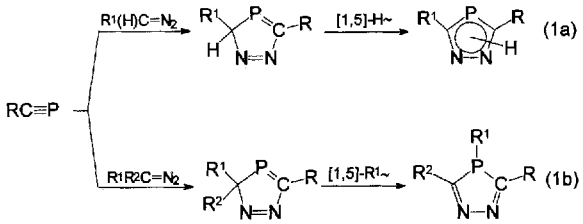
The reaction of the (diisopropylamino)phosphaethyne (**1**) with diazo compounds of the type $R^1R^2C{=}N_2$ (**2a–2c**) unexpectedly leads in high yields (60–90%) to the 1-aza-3,4-diphospholene derivatives **3a–3c**, a new class of heterocycles. NMR investigations of the analogous reaction of **1** with diazocyclopentadiene **2d** show that the multi-step formation of **3a–3c** proceeds via the 1-aza-3,4-diphospholes **6a–6d** as intermediates.

Phosphaalkynes RC≡P exhibit a pronounced reactivity towards 1,3-dipoles and, therefore, undergo [3 + 2] cycloaddition with diazo compounds $R^1(H)C{=}N_2$ or $R^1R^2C{=}N_2$ yielding regiospecifically 1*H*-1,2,4- or 3*H*-1,2,4-diazaphospholes[2].

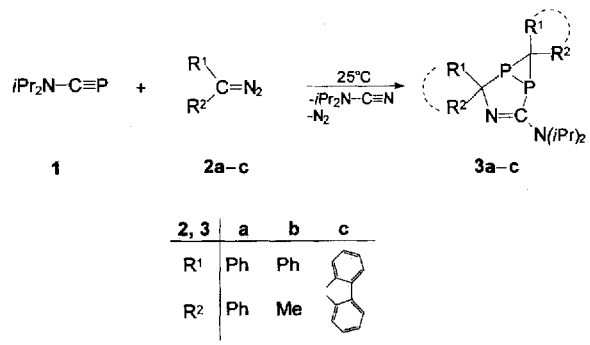
Scheme 1



In order to examine the cycloaddition potential of aminosubstituted phosphaalkynes $R_2N{-}C{\equiv}P$[1,3] in comparison with the alkyl compounds RC≡P we studied reactions of $i\mathrm{Pr}_2N{-}C{\equiv}P$ (**1**) with diazomethane derivatives. With the reactants $R^1(H)C{=}N_2$ the 1,3-dipolar cycloaddition of **1** proceeds as in the case of the alkyl-substituted phosphaalkynes [eq. (1a)] affording 1*H*-1,2,4-diazaphospholes[4], however, with loss of regioselectivity. Hence formation of the regioisomeric 1*H*-1,2,3-diazaphospholes as side products is observed. Using $R^1R^2C{=}N_2$ (**2a–2c**) as 1,3-dipolar reagents, we found a surprising substituent effect for **1** leading to the novel phosphaheterocycles **3a–3c** according to Scheme 2 and not to the expected 3*H*- or 4*H*-1,2,4-diazaphospholes [eq. (1b)].

The reactions of **1** with **2a–2c** take place at 25°C in toluene solution with evolution of N_2 and elimination of $i\mathrm{Pr}_2N{-}C{\equiv}N$ which is collected in a cold trap (−196°C)

Scheme 2



and detected by GC-MS spectroscopy. During this process the color of the reaction mixture changes from red to brown. ^{31}P-NMR control measurements indicate complete consumption of **1** together with an almost quantitative generation of **3a–3c** after 3 to 5 hours. While **3a** and **3c** are stable at room temperature, even in organic solvents, the mixture of the diastereomers **3b** undergoes a slow decomposition in toluene solution giving rise to the formation of a series of unidentified phosphorus-containing compounds.

The molecular structures of **3a–3c** were deduced from spectroscopic investigations and conclusively ascertained by an X-ray diffraction study of single crystals of **3c**. The mass spectra (70 eV) of **3a** and **3c** show the molecular peaks M^+(**3a**) = 520 and M^+(**3c**) = 516 with relative intensities of 52 and 22%, respectively. The ^{31}P resonances of **3a–3c** result from an AB spin system and appear in the high-field region (δ_P = −109.6 to −128.6) with $^1J(P_A,P_B)$ couplings of 190–203 Hz. Chemical shifts and coupling constants are characteristic of diphosphiranes[5], especially for spirocyclic derivatives[6]. Due to the chirality of the P atoms in **3a–3c**

[◇] Part 44: See ref.[1].

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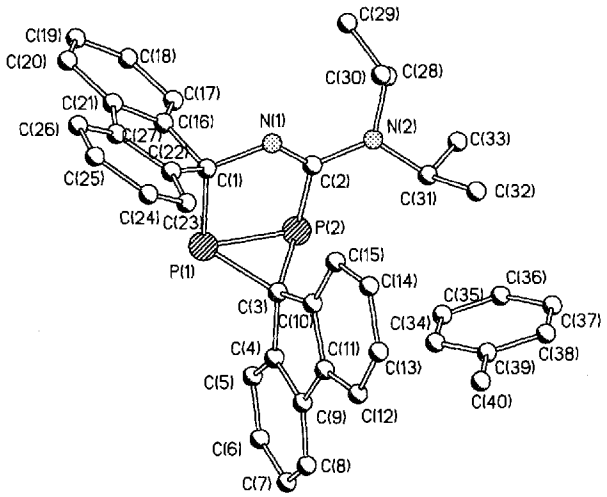
and/or hindered rotation of the amino group around the sp^2 C–N bond, the isopropyl groups, as expected, are magnetically non-equivalent and hence give rise to separate signals both in the ^{1}H- and ^{13}C-NMR spectra (see Experimental). The assumption of a rotational barrier is supported by the observed ^3J[P(2)C(31)] coupling of 18 Hz. The ^{13}C resonance of the N-sp^2-C atom as usual is found at $\delta \approx 165$.

Final proof of the structures of **3a–3c** comes from an X-ray diffraction study of product **3c** obtained from **1** and 9-diazofluorene **2c**. The polycyclic system contains a hitherto unknown 1-aza-3,4-diphospholene unit in the center of the molecule (Figure 1). The two P atoms also belong to the diphosphirane ring with an almost perpendicular orientation with respect to the azadiphospholene ring plane.

Figure 1. Molecular structure of **3c**[a]



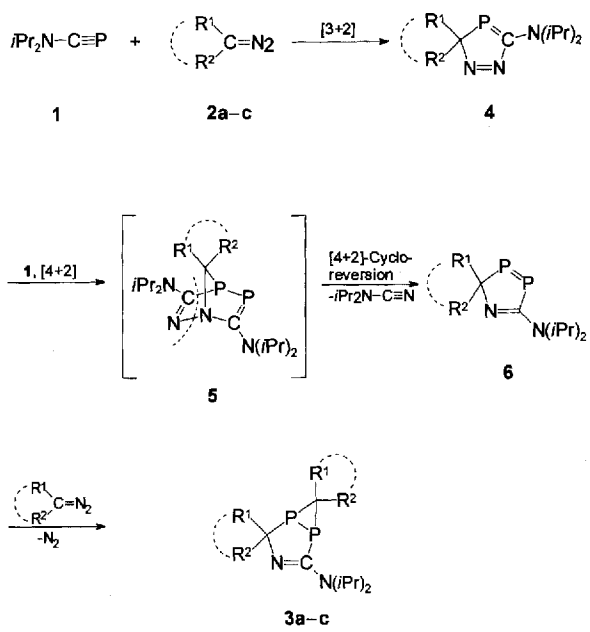
[a] Selected bond lengths [Å] and angles [°]: P1–P2 2.185(2), P1–C1 1.903(5), P2–C2 1.866(6), P1–C3 1.884(5), P2–C3 1.874(5), N1–C1 1.482(6), N1–C2 1.252(6), N2–C2 1.399(7), N2–C28 1.473(6), N2–C31 1.477(6); C1–P1–P2 92.7(2), C1–P1–C3 107.9(2), P2–P1–C3 54.2(2), C2–P2–P1 90.1(2), C2–P2–C3 95.5(2), P1–P2–C3 54.6(2), P1–C3–P2 71.1(2), P1–C1–N1 112.9(3), C1–N1–C2 116.0(5), P2–C2–N1 124.4(5), P2–C2–N2 115.3(4), N1–C2–N2 120.2(5), C2–N2–C28 121.0(4), C2–N2–C31 122.0(4), C28–N2–C31 116.7(4).

The P(1)–P(2) bond length of 2.185(2) Å and the endocyclic angles of the P(1)P(2)C(3) heterocycle correspond to the typical features of diphosphiranes[5,7]. The same is true for the atomic distances and bond anlges of the 1-aza-3,4-diphospholene fragment of **3c**. The N(2)C_3 group is planar with a short N(2)–C(2) bond of 1.399(7) Å, indicating a partial conjugation of the nitrogen lone pair with the C=N bond [twist angle of the planes N(1)–C(2)–P(2)/N(2)–C(28)–C(31): 19.5°].

To rationalize the unexpected formation of **3a–3c** from **1** and diazomethane derivatives $R^1R^2C{=}N_2$ we assume that the 1,5-sigmatropic R shift [eq. (1b)] of the primary 3*H*-1,2,4-diazaphospholes **4** is excluded by the preference of the [4 + 2] cycloaddition of a further molecule of **1** to the PC double bond of **4** (Scheme 3).

The bicyclic systems **5** formed as intermediates spontaneously eliminate diisopropylaminonitrile $iPr_2N{-}C{\equiv}N$ in a [4 + 2] cycloreversion reaction affording the corresponding substituted 1-aza-3,4-diphospholes **6** with a highly reactive diphosphene unit. Similar hetero Diels-Alder reactions of 1,3-azaphosphinines with alkynes or of 1,3-aza-arsinines with tBuC≡P followed by cycloreversion with benzonitrile elimination to give phosphinines and 1,3-phosphaarsinines, respectively, were recently observed by Märkl et al.[8].

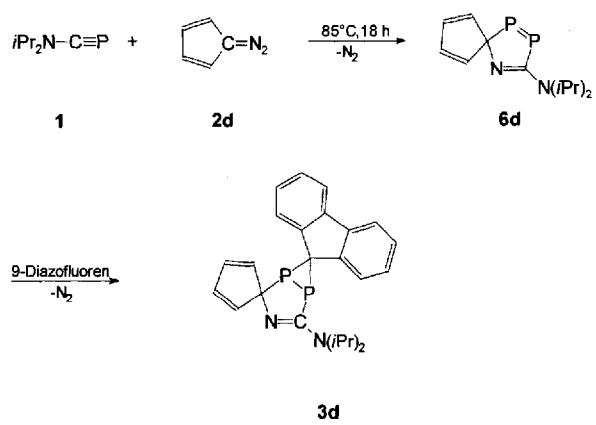
Scheme 3



The diphospholes **6** contain a $\lambda^3\sigma^2$-P/$\lambda^3\sigma^2$-P bond and belong to the fairly new class of 1,2-diphospholes[9]. In agreement with the easily practicable [3 + 2] cycloaddition of diazo compounds to diphosphenes[10] compounds **6** react with **2a–2c** with N_2 elimination to give the final products **3a–3c**.

The mechanistic interpretation presented above for the multistep formation of **3a–3c** is strongly supported by a close inspection of the reaction of **1** with diazocyclopentadiene **2d** which after 18 hours at 85 °C yielded the 1,2-diphosphole derivative **6d** (Scheme 4) instead of the 1-aza-3,4-diphospholene analogue expected according to Scheme 2.

Scheme 4



The $^{31}P\{^1H\}$-NMR spectrum of **6d** shows two AB doublets at low field (δ_P = 336.6, 318.0) with a very large $^1J(P_A,P_B)$ coupling of 535.6 Hz. Beyond doubt these data indicate a PP double bond with *cis* configuration of the substituents[11] and are characteristic of a 1,2-diphosphole unit[9]. The ^1H- and ^{13}C NMR values of **6d** also are in good accord with the proposed constitution.

The stability of **6d** can be attributed to the fact that the diazocyclopentadiene **2d** is less reactive than the 1,3-dipolar reagents **2a**–**2c**. Therefore, the expected [3 + 2] cycloaddition of **2d** to **6d** followed by N_2 elimination does not occur in this special case. This explanation of the experimental result proved right by the reaction of **6d** with 9-diazofluorene **2c** yielding the expected 1-aza-3,4-diphospholene derivative **3d**.

In conclusion, the results presented in this paper suggest that reactions of aminophosphaalkynes with secondary diazo compounds may be a general route to 1-aza-3,4-diphospholene derivatives, a new class of heterocycles. Their formation can be attributed to the particular electronic structures of $R_2NC{\equiv}P$ and the first step products 3*H*-1,2,4-diazophospholes giving preference to a hetero Diels-Alder reaction over the 1,5-substituent migration usually observed for the [3 + 2] cycloadducts of *t*BuC≡P. The final products result from a [4 + 2] cycloreversion with elimination of R_2NCN, in case of the more reactive diazo compounds followed by a further [3 + 2] cycloaddition and N_2 elimination.

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Experimental

All reactions were carried out by using a standard vacuum line. Reaction vessels were either Schlenk flasks or ampoules with several break seals and an NMR tube. Solvents and deuterated compounds for NMR measurements were carefully dried and degassed. 2-Diisopropylamino-1-phosphaethyne (**1**)[3a] and the diazo compounds **2a**–**2d**[12] were prepared by published methods. – NMR: Bruker AC 200 (200.13 MHz, ^1H, Standard: TMS; 81.02 MHz, ^{31}P, Standard: 85% H_3PO_4; 50.32 MHz, ^{13}C, Standard: TMS). – MS (EI): Model CH5 MAT-Finnigan.

Standard Procedure for the Preparation of the 1-Aza-3,4-diphospholenes **3a**–**3c** *and the 1-Aza-3,4-diphosphole* (**6d**): To a solution of 1.0 mmol of the corresponding diazo compound (**2a**–**2c**) in toluene or diethyl ether (5 ml) prepared in a 50-ml Schlenk flask 143 mg (1.0 mmol) of $iPr_2NC{\equiv}P$ (**1**) was added by vacuum condensation at −196 °C. The mixture was stirred during slow warming of the mixture up to 20 °C. A steady color change from wine-red to red-brown was observed together with the evolution of N_2. ^{31}P-NMR control measurements indicated a complete consumption of **1** after 3 (**2a**, **2b**) and 5 h (**2c**) and the formation of **3a**–**3c**. **3a** and **3b** were the only P-containing products of the respective reactions, whereas in case of **3c** some side products were detected by ^{31}P-NMR. The volume of the reaction mixture was reduced to 1.5 ml by evaporation of the solvent under vacuum and the mixture was stored at −25 °C. After 3 to 4 days pale yellow crystals precipitated from the solution of **3c**. The crystal structure analysis of **3c** revealed the presence of 1 equivalent of toluene per formula unit. **3a** and **3b** were obtained as red oils. A toluene solution of **3b** undergoes decomposition within 30 minutes at 25 °C (observed during the ^{13}C-NMR investigation). Yields: **3a**, 92%; **3b**, 87%; **3c**, 60%.

The analogous reaction of **1** with diazocyclopentadiene **2d** only occurred on heating of the mixture at 85 °C. Stirring was continued for 18 h at this temperature, and then all volatile components (unreacted **1** or **2d**, toluene, diisopropylaminonitrile) were removed by vacuum condensation. The non volatile residue was extracted several times with 5 ml of pentane. The combined pentane fractions were filtered to remove insoluble particles. Then the solvent was evaporated from the filtrate furnishing **6d** as a yellow oil in 10% yield.

1-Aza-3,4-diphospholene (**3a**): ^1H NMR ($CDCl_3$): δ = 0.9 (d, *J* = 6.5 Hz, 3H, CH_3), 1.1 (d, *J* = 6.5 Hz, 6H, CH_3), 1.3 (d, *J* = 6.5 Hz, 3H, CH_3), 3.2 [sept, *J* = 6.5 Hz, 1H, $CH(CH_3)_2$], 4.9 [sept, *J* = 6.5 Hz, 1H, $CH(CH_3)_2$], 6.7–7.4 (m, 20H, C_6H_5). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −112.7 [d, ^1J(P,P) = 201.0 Hz, 1 P, P_A], −119.1 [d, ^1J(P,P) = 201.0 Hz, 1 P, P_B]. – ^{13}C NMR ($CDCl_3$): δ = 20.8 (s, CH_3), 21.1 (s, CH_3), 22.0 (s, CH_3), 22.1 (s, CH_3), 47.6 (m, CH), 55.3 [dd, ^3J(P,C) = 27.0, ^4J(P,C) = 7.5 Hz, CH], 125.0–132.2 (C_6H_5), 163.0 [dd, ^1J(P,C) = 60.0, ^2J(P,C) = 4.5 Hz, C=N). – MS (70 eV); *m/z* (%): 520 (52) [M^+], 477 (1) [$M^+ - C_3H_7$], 421 (83) [$M^+ - NC_6H_{13}$], 323 (66) [$M^+ - 2\,C_6H_5 - C_3H_7$], 167 (100) [$M^+ - 4\,C_6H_5 - 3\,CH_3$].

1-Aza-3,4-diphospholene (**3b**): 2 Isomers (ratio ca. 1:1). – ^1H NMR ($CDCl_3$): δ = 0.5–1.3 (18H, CH_3), 3.2–4.4 [2H, $CH(CH_3)_2$], 6.2–7.5 (m, 10H, C_6H_5). – $^{31}P\{^1H\}$ NMR: δ = −118.4 [d, ^1J(P,P) = 198 Hz, 1 P, P_A of isomer **a**], −120.6 [d, ^1J(P,P) = 198 Hz, 1 P, P_B of isomer **a**]; −122.8 [d, ^1J(P,P) = 190 Hz, 1 P, P_A of isomer **b**], −128.6 [d, ^1J(P,P) = 190 Hz, 1 P, P_B of isomer **b**].

1-Aza-3,4-diphospholene (**3c**): ^1H NMR ($CDCl_3$): δ = 0.8 (d, *J* = 6.5 Hz, 3H, CH_3), 1.0 (d, *J* = 5.0 Hz, 6H, CH_3), 1.3 (d, *J* = 6.7 Hz, 3H, CH_3), 3.5 [sept, *J* = 6.5 Hz, 1H, $CH(CH_3)_2$], 4.4 [sept, *J* = 5.0 Hz, 1H, $CH(CH_3)_2$] 6.7–8.2 (m, 16H, arom. H). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −109.6 [d, ^1J(P,P) = 203 Hz, 1 P, P_A], −112.0 [d, ^1J(P,P) = 203 Hz, 1 P, P_B]. – ^{13}C NMR ($CDCl_3$): δ = 20.0 (s, CH_3), 21.2 (s, CH_3), 21.5 (s, CH_3), 21.6 (s, CH_3), 48.5 [s, $CH(CH_3)_2$], 56.2 [d, ^3J(P,C) = 18.0 Hz, $CH(CH_3)_2$]; aromatic C: 119.4(s), 120.0(s), 120.2(s), 120.4(s), 120.8 [d, J(P,C) = 11.2 Hz], 121.4 [d, *J*(P,C) = 8.9 Hz], 121.8 [d, *J*(P,C) = 8.2 Hz], 123.5 [dd, *J*(P,C) = 3.7; 4.1 Hz], 124.3(s), 124.8(s), 125.8(s), 126.0(s), 126.4(s), 126.5(s), 126.7(s), 127.8(s), 137.2(s), 139.6 [dd, *J*(P,C) = 7.0; 3.0 Hz], 142.0(s), 142.9 [d, *J*(P,C) = 1.9 Hz], 146.6 [d, *J*(P,C) = 13.9 Hz], 146.9 [d, *J*(P,C) = 3.9 Hz], 148.5 [d, *J*(P,C) = 12.5 Hz], 148.8 [d, *J*(P,C) = 12.3 Hz]; 168.0 [dd, ^1J(P,C) = 54.0, ^2J(P,C) = 15.0 Hz, C=N]. – MS (70 eV); *m/z* (%): 516 (22) [M^+], 486 (1) [$M^+ - 2\,CH_3$], 352(17) [$M^+ - C_{13}H_8$]. – $C_{40}H_{38}N_2P_2$ (608.66): calcd. C 78.93, H 6.29, N 4.60; found C 78.92, H 6.25, N 4.66.

1-Aza-3,4-diphosphole (**6d**): ^1H NMR ($CDCl_3$): δ = 1.1 (d, ^3J(H,H) = 6.5 Hz, 6H, CH_3), 1.3 (d, ^3J(H,H) = 7.0 Hz, 6H, CH_3), 3.6 [sept, ^3J(H,H) = 6.5 Hz, 1H, $CH(CH_3)_2$], 3.7 [sept, ^3J(H,H) = 7.0 Hz, 1H, $CH(CH_3)_2$], 6.5 (m, 4H, HC=). – ^{31}P NMR ($CDCl_3$): δ = 318.0 [d, ^1J(P,P) = 535.6 Hz, 1 P, P_A], 336.6 [d, ^1J(P,P) = 535.6 Hz, 1 P, P_B]. – ^{13}C NMR ($CDCl_3$): δ = 21.5 [d, ^4J(P,C) = 2.9 Hz, CH_3], 21.6 [d, ^4J(P,C) = 3.2 Hz, CH_3], 51.4 [d, ^3J(P,C) = 6.1 Hz, $CH(CH_3)_2$], 51.6 [d, ^3J(P,C) = 6.0 Hz, $CH(CH_3)_2$], 128.3 (br., quart. C), 133.2 [d, ^3J(P,C) = 3 Hz, HC=C], 133.4 [d, ^3J(P,C) = 3 Hz, HC=C], 135.0 [d, ^2J(P,C) = 3 Hz, HC=C), 135.1 [d, ^2J(P,C) = 2 Hz, HC=C], 155.6 [dd, ^1J(P,C) = 23.0, ^2J(P,C) = 8.0 Hz, C=N].

Reaction of **6d** *with* **2c**: To a toluene solution of **6d** prepared from **1** and **2d** as described above 9-diazofluorene **2c** was added at 25°C. After stirring for 2 d, the resulting product **3d** was characterized by NMR spectroscopic investigations. – ^{1}H NMR ($CDCl_3$): δ = 1.3 (d, J = 6.3 Hz, 3H, CH_3), 1.5 (d, J = 6.5 Hz, 6H, 2 CH_3), 1.8 (d, J = 7.0 Hz, 3H, CH_3), 3.9 [m, 1H, $CH(CH_3)_2$], 4.9 [m, 1H, $CH(CH_3)_2$], 7.0–8.8 (m, 12H, sp^2-CH). – ^{31}P NMR ($CDCl_3$): δ = –79.4 [d, ^1J(P,P) = 156.4 Hz, 1 P, P_A], –85.2 [d, ^1J(P,P) = 156.4 Hz, 1 P, P_B].

X-ray Crystal Structure Analysis[13] *of* **3c**: SYNTEX $P2_1$, radiation: Mo-K_α (λ = 0.71073 Å), T = 153 K; $C_{33}H_{30}N_2P_2 \cdot C_7H_8$; M = 608.66 g/mol; crystal size 0.21 × 0.34 × 0.1 mm; monoclinic, space group: $P2_1/n$; a = 10.948(5), b = 9.983(5), c = 29.53(2) Å, β = 91.14(5)°; V = 3227(3) Å^3; Z = 4; d_{calcd} = 1.249 Mg/m^3; μ = 0.166 mm^{-1}. F(000) = 1280; Θ range 2.15–22.04°, index ranges: $0 \leq h \leq 11$, $0 \leq k \leq 10$, $-31 \leq l \leq 31$; reflections collected: 4226, independent reflections: 3976 [R(int) = 0.0580]; Data/restraints/parameters: 3976/0/397; Solution: direct methods; refinement method: Full-matrix least-squares on F^2 (SHELXL-93[14]); R indices (all data): $R1$ = 0.1320, $wR2$ = 0.1299; final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0554, $wR2$ = 0.1108; GoF on F^2: 0.820.

☆ Dedicated to Professor *Max Herberhold* on the occasion of his 60th birthday.

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