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One-pot microwave synthesis of tertiary phosphine sulfides directly from aromatic alkenes, elemental phosphorus and sulfur in KOH-DMSO system

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One-pot microwave synthesis of tertiary phosphine sulfides directly from aromatic alkenes, elemental phosphorus and sulfur in KOH–DMSO system

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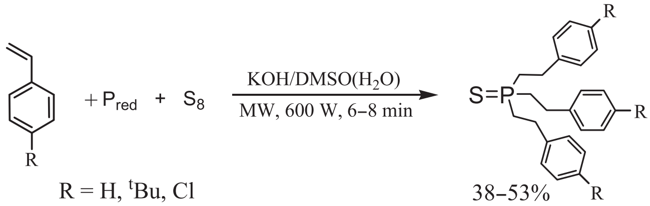
Aromatic alkenes (vinylbenzene, 1-(*tert*-butyl)-4-vinylbenzene, 1-chloro-4-vinylbenzene) react with red phosphorus and elemental sulfur in the superbasic system KOH–DMSO(H_2O) under microwave irradiation (600 W, 6–8 min, Ar) in the presence of hydroquinone to afford tris(2-phenylethyl)-, tris[2-(4-^{t}Bu-phenyl)ethyl]- and tris[2-(4-Cl-phenyl)ethyl]phosphine sulfides in 53%, 38% and 42% yield, respectively.



Keywords: aromatic alkenes; red phosphorus; elemental sulfur; microwave irradiation; tertiary phosphine sulfides

1. Introduction

Tertiary phosphine sulfides find application as extractants for noble rare-earth metals and radionuclides,[1–4] modifiers for synthetic rubbers and petroleum resins,[5] surfactants, chemical sensitizers in photographic materials,[6–11] additives to lubricating oils and electrolytes,[12] adhesive compositions,[13] as well as components of insect repellents, insecticides and fungicides. The functional P=S group constitutes an important part of some pharmacophores.[14,15] Tertiary phosphine sulfides are also used as ligands in the design of new metal complex catalysts [16–25] showing, in some cases, better catalytic activity than that of the complexes with tertiary phosphines [20,22]. In several reactions, tertiary phosphine sulfides are employed as co-catalysts.[26,27] Apart from that, phosphine sulfides are valuable building blocks in the synthesis

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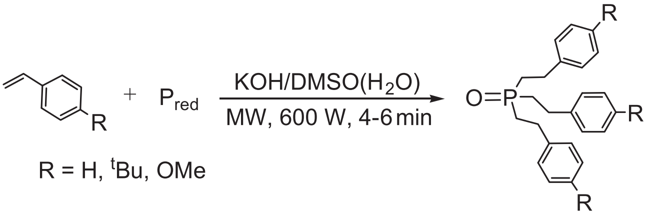
*Corresponding author. Email: boris_trofimov@irioch.irk.ru of corresponding tertiary phosphines,[28] as well as co-reagents for the preparation of CdS–CdSe nanocrystal dots and rods.[29]

A number of methods have been proposed for the synthesis of tertiary phosphine sulfides. In general, they are prepared by the reaction of $S{=}PCl_3$ with organometallic reagents.[30] Among other methods for their synthesis are oxidation of the tertiary phosphines with elemental sulfur or reoxidation of tertiary phosphine oxides with less accessible sulfurizing reactants such as B_2S_3,[31] P_2S_5,[32] Lawesson's reagent,[33–38] and $POCl_3$–H_2S.[39,40]

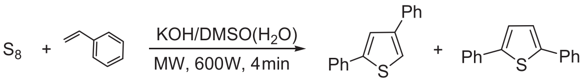
Here, we report a new approach for the synthesis of tertiary phosphine sulfides via one-pot reaction of aromatic alkenes with red phosphorus and elemental sulfur in the superbase multicomponent suspension KOH–DMSO.

It is known [41–43] that aromatic alkenes are phosphorylated with the triad P_{red}–KOH–DMSO(H_2O) at 90–130°C for 3 h to form tertiary phosphine oxides in 30–77% yields. Using microwave irradiation the reaction affords the phosphine oxides in 82–85% yields in 4–6 min [41–43] (Scheme 1).



Scheme 1. Reaction of red phosphorus with aromatic alkenes in the KOH–DMSO system under microwave assistance.

Elemental sulfur alone also reacts with vinylbenzene in the KOH–DMSO–H_2O suspension under microwave irradiation (600 W, 4 min) to give 2,4- and 2,5-diphenylthiophenes in 30% total yield [44] (Scheme 2).



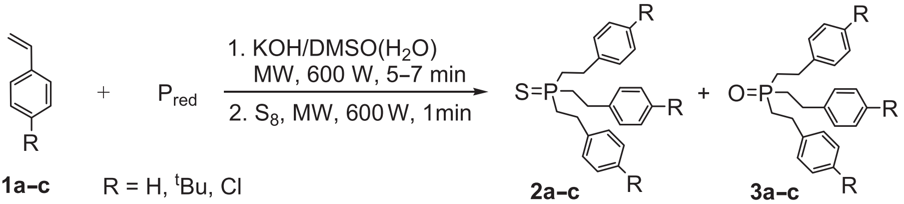
Scheme 2. Reaction of elemental sulfur with vinylbenzene in the KOH–DMSO system under microwave assistance.

The three-component reaction between aromatic alkenes, red phosphorus and elemental sulfur had not been previously reported in the literature.

2. Results and discussion

Aromatic alkenes **1a–c** were shown to react with red phosphorus and elemental sulfur (1:1:1 molar ratio) in the superbasic system KOH–DMSO(H_2O) under microwave irradiation (600 W, 6–8 min, Ar, hydroquinone, as a radical processes inhibitor) to afford tris(2-phenylethyl)-, tris[2-(4-^{t}Bu-phenyl)ethyl]- and tris[2-(4-Cl-phenyl)ethyl]phosphine sulfides **2a–c** in 53%, 38% and 42% yields, respectively (Table 1). Noteworthy, it was necessary to introduce sulfur to the reaction mixture in a second step 5–7 min after the alkene **1**–P_{red}–KOH–MSO–(H_2O) suspension was

Table 1. One-pot reaction of aromatic alkenes with red phosphorus and sulfur in a KOH–DMSO suspension.[a]

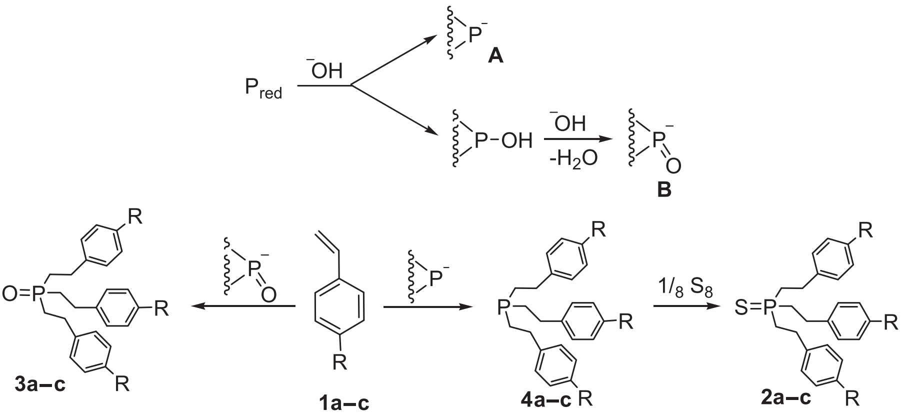


Aromatic alkenes **1a**–**c** (mmol)	P_{red}, mmol	S_8, mmol	KOH, mmol	Products **2, 3** (their molar ratio)[b]	Yield of **2**, %[c]
$PhCH{=}CH_2$, **1a** (100)	100	100	178.5	**2a,3a** (2.3:1)	**2a**, 53
4-$^tBuC_6H_4CH{=}CH_2$, **1b** (30.0)	32.2	30.0	89.2	**2b,3b** (4.5:1)	**2b**, 38
4-$ClC_6H_4CH{=}CH_2$, **1c** (7.2)	7.0	7.2	12.5	**2c,3c** (1.4:1)	**2c**, 42

[a] All steps of the experiments were carried out under microwave irradiation (600 W, 6–8 min) in argon atmosphere.
[b] Molar ratio of the compounds **2** and **3** were calculated from the ^{31}P NMR spectra of the crude products. In the reaction mixture formed at the first step of the reaction (before addition of elemental sulfur), the corresponding tertiary phosphines **4a**–**c** were also detected (^{31}P NMR data).
[c] Isolated yield.

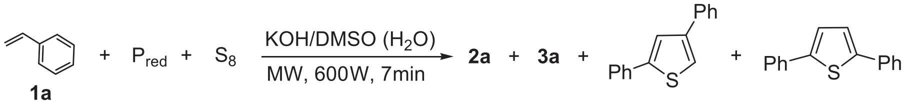
irradiated. The process was finished after an additional 1 min of MW-irradiation. Under these conditions the corresponding tertiary phosphine oxides **3a**–**c** are also formed (Table 1).

Cleavage of the P–P bonds in red phosphorus with hydroxide anions [45] is a key step in this new reaction. This step is likely to form highly active P-centered nucleophiles such as polyphosphide **A** and polyphosphinite **B** anions. These anions then subsequently react with electrophiles **1a**–**c** to give tertiary phosphines **4a**–**c** or phosphine oxides **3a**–**c**. The phosphines **4a**–**c** are further sulfurized by elemental sulfur to afford phosphine sulfides **2a**–**c** (Scheme 3).



Scheme 3. Plausible mechanism for the multi-component reaction between aromatic alkenes, red phosphorus and elemental sulfur in the KOH–DMSO(H_2O) system.

Using vinylbenzene as an example, it has been shown that simultaneous irradiation (600 W, 7 min, Ar) of all of the components of the reaction mixture (**1a**–P_{red}–S_8–KOH–DMSO–H_2O–hydroquinone) decreases the total yield of phosphine chalcogenides, **2a** and **3a**, down to ∼33% (their molar ratio 1:1.5) as well as producing 2,4- and 2,5-diphenylthiophenes in 21% total yield (data of mass spectrometry) (Scheme 4).



Scheme 4. Simultaneous irradiation of vinylbenzene, red phosphorus and elemental sulfur in the KOH–DMSO suspension.

Without microwave activation, the reaction between vinylbenzene, red phosphorus and elemental sulfur proceeds in the KOH–DMSO(H_2O) suspension upon heating (90–95°C) for 3 h to give phosphine sulfide **2a** and phosphine oxide **3a** in a 49% total yield (their molar ratio ~1:10).

The addition of elemental sulfur to a pre-heated (90–95°C) suspension of vinylbenzene–P_{red}–S_8–KOH–DMSO–H_2O–hydroquinone via three portions in 20 min equal time spans and subsequent additional heating of the resultant reaction mixture (90–95°C, 2 h) affords phosphine sulfide **2a** and phosphine oxide **3a** in a 57% total yield (their molar ratio ~1:1).

It has been reported,[46] that tris(2-phenylethyl)phosphine chalcogenides **2a** and **3a** are effective extracting agents of gold from low-acidic solutions. Additionally, phosphine sulfide **2a** is known to exert high extracting ability towards silver.[46]

In addition, we have found that phosphine sulfide **2a** or its mixture with phosphine oxide **3a** (~1:1) can be successfully employed for extraction of palladium, platinum, lead and cadmium from hydrochloride solutions. These investigations are now under way and their results will be published as a full paper elsewhere.

3. Conclusion

Thus, we have developed a straightforward facile synthesis of tertiary phosphine sulfides *via* the one-pot multi-component reaction of aromatic alkenes, red phosphorus and elemental sulfur in the KOH–DMSO(H_2O) system. The reaction is activated by MW-irradiation to afford the target compounds in good yields. The synthesized tertiary phosphine sulfides are effective extractants of diverse metals, prospective ligands for metal complexes, modifiers for synthetic rubbers and petroleum resins, additives to lubricating oils and electrolytes, precursors to agrochemicals and building blocks for organic synthesis.

4. Experimental

4.1. *General*

Melting points (uncorrected) were measured on a Kofler micro hot-stage apparatus. The microanalyses were performed on a Thermo Scientific Flash 2000 organic element analyzer. Fourier transform IR spectra were run on a Bruker Vertex 70 instrument. Raman spectra were run on a Varian FT-Raman. The ^{1}H, ^{13}C and ^{31}P spectra were recorded on a BrukerAV-400 spectrometer (400.13, 100.61 and 161.98 MHz, respectively) and referenced to H_3PO_4 (^{31}P NMR). Chemical shifts (δ) are expressed in ppm downfield from hexamethyldisiloxane, $CHCl_3$ as internal standards. One should note that phosphine sulfides **2a,c** were spectrally characterized in this paper for the first time. All steps of the experiment were carried out in argon atmosphere. Red phosphorus (KSAN “SIA”), 1-(*tert*-butyl)-4-vinylbenzene (Alfa-Aesar), 1-(chloro)-4-vinylbenzene (Alfa-Aesar), KOH (~15% water content) and DMSO (1% water content) were used as purchased.

The MW-assisted reactions were carried out in a microwave reactor Samsung M181DNR (max power level 850 W) equipped with reflux condenser. Mass spectra were run on a Hewlett-Packard HP-5971A instrument with EI ionization (70 eV).

4.2. *Synthesis of tertiary phosphine sulfides from aromatic alkenes, red phosphorus and elemental sulfur in the KOH–DMSO under microwave irradiation*

4.2.1. *Tris(2-phenethyl)phosphine sulfide (**2a**)*

A mixture of the vinylbenzene **1a** (10.45 g, 100.0 mmol) and red phosphorus (3.10 g, 100 mmol), hydroquinone (0.10 g), KOH (10.00 g, 178.5 mmol), water (1.5 ml) and DMSO (40 ml) was irradiated (600 W, temperature reached 190–200°C) for 7 min. Then elemental sulfur (3.2 g, 100.0 mmol) was added and the reaction mixture was irradiated for 1 min additionally. The reaction mixture was cooled, diluted with water (60 ml), the unreacted red phosphorus was filtered off and the filtrate was extracted with benzene (3 × 20 ml). The combined benzene extracts were washed with 5% NaOH aq. solution and 10% KCl aq. solution (3 × 20 ml) and dried over K_2CO_3. The benzene was removed under vacuum. The ^{31}P NMR spectrum of the residue contains the following signals: 48.44 ppm (phosphine sulfide **2a**) and 47.85 ppm (phosphine oxide **3a**). According to ^{31}P NMR, molar ratio **2a**:**3a** ~2.3:1. The resulting product so obtained was precipitated from dichloromethane with hexane twice to afford 6.70 g of phosphine sulfide of **3a** (yield 53%).

White powder; yield: 6.70 g (53%); mp 96°C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.11 - 2.17$ (m, 6 H, CH_2P), 2.89–2.99 (m, 6 H, CH_2Ph), 7.16 and 7.23 (m, 15 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 28.57$ (d, $^2J_{CP} = 2.7$ Hz, $\underline{C}H_2Ph$), 32.84 (d, $^1J_{CP} = 47.9$ Hz, CH_2P), 126.52 ($p{-}C_{Ph}$), 128.19 ($o{-}C_{Ph}$), 128.68 ($m{-}C_{Ph}$), 140.52 (d, $^3J_{CP} = 13.4$ Hz, $i{-}C_{Ph}$). ^{31}P NMR (161.98 Hz, $CDCl_3$): $\delta = 48.74$. IR (KBr, ν, cm^{-1}): 3105, 3084, 3061, 2930, 3001, 2930, 1601, 1496, 1453, 1401, 1297, 1270, 1226, 1216, 1208, 1173, 1159, 1136, 1070, 1029, 1013, 960, 944, 911, 836, 774, 768, 753, 720, 706, 697, 621, 607, 543, 498. Raman (150 mw, solid, ν, cm^{-1}): 3053, 3037, 2934, 2903, 2868, 1603, 1584, 1450, 1403, 1208, 1180, 1159, 1031, 1004, 829, 623, 598, 544, 500, 475, 218.

Anal. Calc. for $C_{24}H_{27}PS$ (378.51): C, 76.16; H, 7,19; P, 8.18; S, 8.47. Found: C, 76.28; H, 7.09; P, 7.99; S, 8.35%.

4.2.2. *Tris[4-(tert-butyl)phenethyl]phosphine sulfide (**2b**)*

A mixture of the 1-(*tert*-butyl)-4-vinylbenzene **1b** (4.80 g, 30.0 mmol) and red phosphorus (1.0 g, 32.2 mmol), hydroquinone (0.10 g), KOH (5.00 g, 89.2 mmol), water (0.75 ml), and DMSO (20 ml) was irradiated (600 W, temperature reached 190–200) for 7 min. Then elemental sulfur (0.96 g, 30.0 mmol) was added and the reaction mixture was irradiated for 1 min additionally. The reaction mixture was cooled, diluted with water (30 ml), the unreacted red phosphorus was filtered off and the filtrate was extracted with benzene (3 × 10 ml). The combined benzene extracts were washed with 5% NaOH aq. solution and 10% KCl aq. solution (3 × 10 ml) and dried over K_2CO_3. The benzene was removed under vacuum. The ^{31}P NMR spectrum of the residue contains the following signals: 48.94 ppm (phosphine sulfide **2b**) and 47.78 ppm (phosphine oxide **3b**). According to ^{31}P NMR, molar ratio **2b**:**3b** ~4.5:1. The residue was treated in cold methanol (10 × 3 ml) and the insoluble white powder was filtered off on Schott filter, dried in vacuum to afford 2.07 g of**2b** (38%).

White powder; yield: 2.07 g (38%); mp 145–146°C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.31$ (s, 27 H, Me), 2.11–2.15 (m, 6 H, CH_2P), 2.91-2.93 (m, 6 H, $C\underline{H}_2C_6H_4$), 7.12 and 7.32 (m, 12 H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$) : $\delta = 28.17$ (d, $^2J_{CP} = 2.0$ Hz, $\underline{C}H_2Ph$), 31.44 (Me), 32.80 (d, ${}^{1}J_{CP} = 47.7$ Hz, CH_2P), 34.47 (<u>C</u>Me), 125.70 (o–C_{Ar}), 127.68 (m–C_{Ar}), 137.32 (d, ${}^{3}J_{CP} = 13.6$ Hz, i–C_{Ar}), 149.62 (p–C_{Ar}). ^{31}P NMR (161.98 Hz, $CDCl_3$) : $\delta = 48.76$. IR (KBr, ν, cm^{-1}): 3134, 3094, 3057, 2962, 2904, 2865, 1646, 1517, 1474, 1463, 1448, 1414, 1393, 1363, 1269, 1218, 1206, 1143, 1109, 1020, 963, 936, 855, 839, 815, 771, 742, 704, 589, 563, 550, 524. Anal. Calc. for $C_{36}H_{51}PS$ (546.83): C, 79.07; H, 9.40; P, 5.66; S, 5.86. Found: C, 79.15; H, 9.29; P, 5.59; S, 5.75%.

4.2.3. *Tris(4-chlorophenethyl)phosphine sulfide (**2c**)*

A mixture of the 1-(chloro)-4-vinylbenzene **1c** (1 g, 7.25 mmol) and red phosphorus (0.22 g, 7.0 mmol), hydroquinone (0.01 g), KOH (0.70 g, 12.5 mmol), water (0.11 ml) and DMSO (10 ml) was irradiated (600 W, temperature reached 190–200°C) for 5 min. Than elemental sulfur (0.23 g, 7.25 mmol) was added and the reaction mixture was irradiated for 1 min additionally. The reaction mixture was cooled, diluted with water (15 ml), the unreacted red phosphorus was filtered off and the filtrate was extracted with benzene (3 × 15 ml). The combined benzene extracts were washed with 5% NaOH aq. solution and 10% KCl aq. solution (3 × 5 ml) and dried over $CaCl_2$. The benzene was removed under vacuum. The ^{31}P NMR spectrum of the residue contains the following signals: 48.82 ppm (phosphine sulfide **2c**) and 48.02 ppm (phosphine oxide **3c**). According to ^{31}P NMR, molar ratio **2c**:**3c** ~1.4:1. The residue was recrystallized from hot hexane three times. The residue obtained was dried in vacuum (5 Torr, 30°C) to afford 0.49 g of **3c**.

Pale powder; yield: 0.49 g (42%); mp 120°C (hexane). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.01 - 2.10$ (m, 6 H, CH_2P), 2.83–2.90 (m, 6 H, $CH_2C_6H_4$), 7.08 and 7.23 (m, 12 H, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 28.0$ (d, ${}^{2}J_{CP} = 2.3$ Hz, <u>C</u>$H_2C_6H_4$), 32.82 (d, ${}^{1}J_{CP} = 47.9$ Hz, CH_2P), 128.75 (o–C_{Ar}), 129.52 (m–C_{Ar}), 132.34 (p–C_{Ar}), 138.87 (d, ${}^{3}J_{CP} = 13.0$ Hz, i–C_{Ar}). ^{31}P NMR (161.98 Hz, $CDCl_3$): $\delta = 48.76$. IR (KBr, ν, cm^{-1}): 3084, 3064, 3042, 3026, 2923, 2868, 2858, 1648, 1596, 1575, 1492, 1451, 1433, 1407, 1350, 1269, 1222, 1178, 1148, 1132, 1091, 1042, 1015, 950, 847, 834, 808, 774, 750, 718, 693, 653, 585, 567, 518, 509, 492, 484. Anal. Calc. for $C_{24}H_{24}Cl_3PS$ (481.85): C, 59.82; H, 5.02; Cl, 22.07; P, 6.43; S, 6.65. Found: C, 59.78; H, 5.17; Cl, 22.23; P, 6.59; S, 6.77%.

4.3. *Reaction of vinylbenzene with red phosphorus and elemental sulfur in the KOH–DMSO system at 90–95°C*

(a) A mixture of the vinylbenzene**1a** (2.17 g, 20.8 mmol), red phosphorus (0.62 g, 20 mmol), elemental sulfur (0.70 g, 21.9 mmol), hydroquinone (0.02 g), KOH (2.00 g, 35.7 mmol), water (0.3 ml) and DMSO (8 ml) was stirred for 3 h at 90–95°C. The reaction mixture was cooled, diluted with water (12 ml), the unreacted red phosphorus was filtered off and the filtrate was extracted with benzene (3 × 10 ml). The combined benzene extracts were washed with 5% NaOH aq. solution and 10% KCl aq. solution (3 × 10 ml) and dried over K_2CO_3. The benzene was removed under vacuum to afford 1.27 g of the solid. The ^{31}P NMR spectrum of the latter contains the following signals: 49.28 ppm (phosphine sulfide **2a**) and 48.76 ppm (phosphine oxide **3a**). According to ^{31}P NMR, molar ratio **2a**:**3a** ~1:10, (total yield of **2a** and **3a** ~49%).

(b) A mixture of the vinylbenzene **1a** (10.87 g, 104.4 mmol), red phosphorus (3.10 g, 100 mmol), elemental sulfur (0.50 g), hydroquinone (0.10 g), KOH (10.00 g, 178.5 mmol), water (1.5 ml) and DMSO (40 ml) was stirred for 20 min at 90–95°C. Then to a suspension obtained, equal portions of elemental sulfur (3 × 1 g) were consecutively added for every 20 min. Then the reaction mixture was stirred for 2 h additionally at the same temperature. The reaction mixture was cooled, diluted with water (60 ml), the unreacted red phosphorus was filtered off and the filtrate was extracted with benzene (3 × 20 ml). The combined benzene extracts were washed with 5% NaOH solution and 10% KCl aq. solution (3 × 20 ml) and dried over K_2CO_3. The benzene was removed under vacuum to afford 7.33 g of the solid, the ^{31}P NMR spectrum of which contained the following signals: 48.94 ppm (phosphine sulfide **2a**) and 47.78 ppm (phosphine oxide **3a**). According to ^{31}P NMR, molar ratio **2a**:**3a** ∼1:0.9, (total yield of **2a** and **3a** ∼57%).

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