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Synthesis of unsymmetrical hetaryl-1,2-diketones

Mehman S. Yusubov,[a,*] Galina A. Zholobova,[a] Sergey F. Vasilevsky,[b,†] Eugene V. Tretyakov[b] and David W. Knight[c,‡]

[a]*The Siberian Medical University, 634050 Tomsk, Russian Federation*
[b]*Institute of Chemical Kinetics and Combustion, 630090 Novosibirsk, Russian Federation*
[c]*Department of Chemistry, Cardiff University, P.O. Box 912, Cardiff CF10 3TB, United Kingdom*

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Abstract—Oxidation of the triple bond in 4-alkynylpyrazoles **2a**–**e** and acetylenic derivatives of the crown-ethers **7a**,**b** with $PdCl_2$–DMSO has been carried out to give unsymmetrical hetaryl-1,2-diketones **3a**–**e**; **8a**,**b**. Attempts to oxidize the triple bond in 5-alkynylpyrazole **6** and alkynylpyridines **5a**,**b** and **9** failed. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

1,2-Diketones are of interest in general synthesis[1,2] and for their potential biological activity but have relatively few access routes.[3] This is especially true if the substituent adjacent to the α-dicarbonyl part is a heterocyclic derivative: only a small number of unsymmetrical hetaryl-1,2-diketones are known.[4,5] Data on such unsymmetrical hetaryl-1,2-diketones are scarce. In our opinion, this situation stems primarily from the fact that convenient and versatile procedures for their synthesis are lacking rather these compounds are of little interest. Hence, the major aim of this work was to synthesize unsymmetrical hetaryl-1,2-diketones.

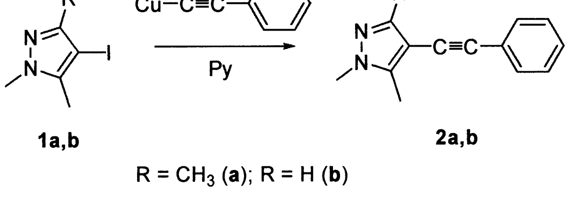
One route to 1,2-diketones which is of particular interest to us is the oxidation of acetylenes to α-diketones using $PdCl_2$–MSO.[6] Whereas the successful use of this method has been demonstrated with a range of simple examples,[7,8] there has been no investigation of this reaction type with alkynylhetarenes so far. Here, we wish to report on the utilization of acetylene derivatives of hetarenes as substrates for this oxidation reaction, with the aim of defining the synthetic utility of this approach for the preparation of unsymmetrical hetaryl-1,2-diketones.

2. Results and discussion

In the synthetic strategy described above, unsymmetrical alkynylhetarenes are the required precursors. Such acetylenic derivatives have typically been prepared by the substitution of a halogen atom in arylhalides by acetylenic moieties. There are two main ways of realizing this conversion. In one of these, the Stephens–Castro method, the reaction is carried out in the presence of copper(I) acetylide.[9] In such cases, the copper ion coordinates to a lone pair of electrons of the halogen atom, facilitating addition of the nucleophilic acetylene to the carbon atom, and expulsion of the halogen anion by the way of ligand coordination with the copper ion. Thus, the copper salt is simultaneously both reactant and catalyst. A second way of activation of halogenoarenes is based on the insertion of metal into the carbon–halogen bond (the Sonogashira method). In this case, the reaction is carried out at the presence of complexes of nickel or palladium,[10,11] sometimes with CuI as a co-catalyst.[12]

It is known that the Pd/Cu-catalyzed Sonogashira cross-coupling of acetylenes with 4-iodopyrazoles, bearing donor substituents, is complicated by reductive deiodination.[13] For this reason 1,3,5-trimethyl-4-phenylethynyl-1*H*-pyrazole (**2a**) and 1,5-dimethyl-4-phenylethynyl-1*H*-pyrazole (**2b**) were synthesized by reaction of corresponding iododerivatives **1a**,**b** with copper(I) phenylacetylide in pyridine by the Stephens–Castro method (Scheme 1).

The alkynylpyrazoles **2c**–**e**, **6** (Schemes 4 and 5) were



Scheme 1.

Keywords: alkynes; oxidation with $PdCl_2$–DMSO; 1,2-diketones.

[*] Corresponding author; e-mail: yusubov@mail.ru

[†] Fax: +73832/342350.

[‡] Fax: +(44)2920/874210.

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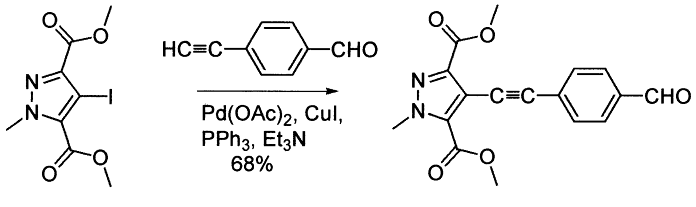
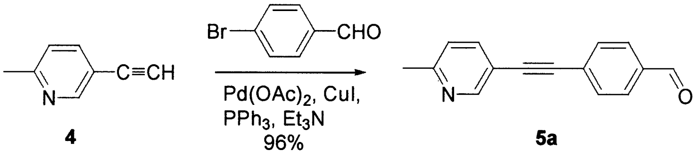


3 **2f**

Scheme 2.



4 **5a**

Scheme 3.

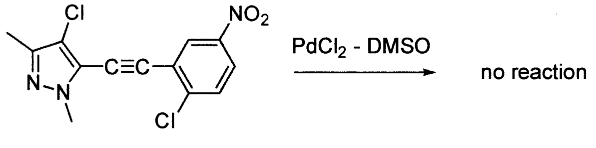
2a-e **3a-e**

Scheme 4. $R^1 = R^2 = R^3 = CH_3$, $R^4 = H$ (**a**); $R^1 = R^3 = CH_3$, $R^2 = R^4 = H$ (**b**); $R^1 = R^2 = R^3 = R^4 = H$ (**c**); $R^1 = R^2 = R^3 = H$, $R^4 = NO_2$ (**d**); $R^1 = CH_3$, $R^2 = NH_2$, $R^3 = H$, $R^4 = OCH_3$ (**e**); $R^1 = CH_3$, $R^2, R^3 = CO_2CH_3$, $R^4 = CHO$ (**f**).

synthesized by a known procedure, and 4-(4-formylphenylethynyl)-1-methyl-1*H*-pyrazole-3,5-dicarboxylic acid dimethyl ester (**2f**) was prepared by Sonogashira cross-coupling of pyrazolyliodide **3** with 4-ethynylbenzaldehyde (Scheme 2).

The synthesis of alkynyl derivatives **7a**,**b** of crown-ethers (Scheme 6) and of alkynylpyridines **5b**, **9** (Scheme 7) has been described elsewhere.[14–17] 4-(6-Methyl-pyridin-3-ylethynyl)-benzaldehyde (**5a**) was prepared in 96% yield also by Sonogashira cross-coupling (Scheme 3).

As a result, alkynyl derivatives having both electron-withdrawing and electron-donating character were to hand. We tried to oxidize these compounds with the reagent combination $PdCl_2$–DMSO.



6

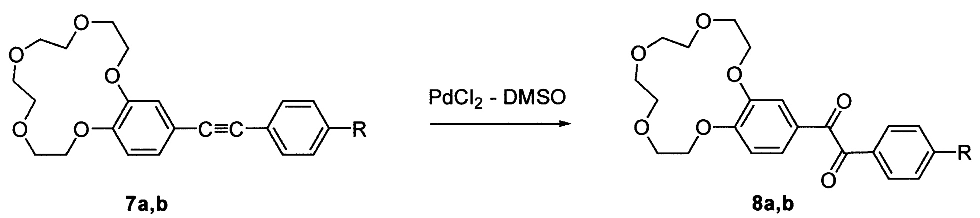
Scheme 5.

We were pleased to find that the pyrazole derivatives **2a**–**e** were regioselectively oxidized with $PdCl_2$–DMSO to give the corresponding α-diketones **3a**–**e** in 55–90% isolated yields (Scheme 4). In contrast to tolane derivatives, bulky electron-donating substituents in vicinal positions to the triple bond did not prevent the oxidation.

The reaction rate was reduced by the influence of electron-withdrawing substituents and the oxidation of 4-alkynylpyrazole **2f** (Scheme 4) failed. For the same reason, the oxidation of the triple bond in 4-chloro-5-(2-chloro-5-nitro-phenylethynyl)-1,3-dimethyl-1*H*-pyrazole (**6**) also failed (Scheme 5).

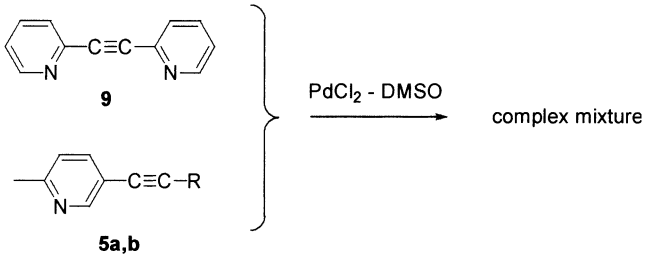
In contrast, the acetylenic derivatives of crown-ethers **7a**,**b** were oxidized very successfully to give the corresponding 1,2-diketones **8a**,**b** in excellent isolated yields (79–84%), after purification by column chromatography (Scheme 6).

The reagent $PdCl_2$–DMSO was ineffective when we tried to oxidize the alkynylpyridine **5a**,**b**; **9**. In these cases, only formation of a complex mixture of reaction products was observed (Scheme 7).



7a,b **8a,b**

Scheme 6. $R = OCH_3$ (**a**), C_6H_5 (**b**).



Scheme 7. R=4-CHO-C_6H_4 (**a**); R=2-Cl-4-NO_2-C_6H_3 (**b**).

In summary, employment of the reagent $PdCl_2$–DMSO permits the regioselective oxidation of triple bond in alkynes substituted with electron-donating groups establishing a convenient route to 1,2-diketones, which are not accessible by any known procedure. The utility of this method for the preparation of new 1,2-diketones can be expected.

3. Experimental

3.1. General

All commercial reagents were used directly as obtained, unless otherwise noted. Compounds **2c**,**d**,[14] **2e**,[13] **5b** and **6**,[15] **7a**,**b**,[16] **9**,[17] and 4-iodo-1-methyl-1*H*-pyrazole-3,5-dicarboxylic acid dimethyl ester (**3**)[19] were prepared by previously reported methods. 4-Iodo-1,5-dimethylpyrazole (**1b**)[19] and 4-iodo-1,3,5-trimethylpyrazole (**1a**)[20] were synthesized by iodination of corresponding alkylpyrazoles as previously described.[18] The chemical names were generated by AutoNom from Beilstein Informationssysteme GmbH. Removal of all solvents was carried out under reduced pressure. Analytical TLC was carried out using Silica gel 60 F_{254} (Merck) and Silica gel 60 G (Merck) was used for column chromatography. IR spectra were obtained for KBr pellets using a Bruker IFS 66 infrared spectrometer. Melting points were obtained using a Kofler melting point apparatus. Microanalyses were obtained using a Hewlett Packard 185 analyzer and a Carlo Erba 1106 analyzer. ^{1}H NMR spectra were recorded on a Bruker Avance 300 spectrometer locked to the deuterium resonance of the solvent. Chemical shifts were calculated relative to solvent signals used as the internal standards: δ_H 7.240 ppm for $CDCl_3$, δ_H 2.50 ppm for DMSO-d_6.

3.1.1. 1,3,5-Trimethyl-4-phenylethynyl-1*H*-pyrazole (2a). 4-Iodo-1,3,5-trimethylpyrazole (**1a**) (1.05 g, 4.44 mmol) and copper(I) phenylacetylide (0.82 g, 4.97 mmol) were refluxed together in pyridine (15 ml) under an argon stream for 8 h, then cooled and diluted with water (50 ml). The resulting solid was filtered off and purified by column chromatography on alumina (benzene) to give alkynylpyrazole **2a** (0.45 g, 48%) as a colorless crystalline solid, mp 53–54°C (hexane); IR: ν_{max}=2225 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H, 3-CH_3), 2.28 (s, 3H, 5-CH_3), 3.71 (s, 3H, N–CH_3), 7.20–7.46 (m, 5H, Ph). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.2; H, 6.8; N, 13.1.

3.1.2. 1,5-Dimethyl-4-phenylethynyl-1*H*-pyrazole (2b). 4-Iodo-1,5-dimethylpyrazole (**1b**) (0.25 g, 1.13 mmol) and copper(I) phenylacetylide (0.2 g, 1.21 mmol) were refluxed together in pyridine (15 ml) under an argon stream for 6 h. After workup as described for the alkynylpyrazole **2a**, the crude product was recrystallized from hexane to give alkynylpyrazole **2b** (0.15 g, 63%) as colorless crystals, mp 42–43°C (hexane); IR: ν_{max}=2228 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H, 5-CH_3), 3.73 (s, 3H, N–CH_3), 7.13 (s, 1H, pyrazole-H^3), 7.24–7.46 (m, 5H, Ph). Anal. Calcd for $C_{13}H_{12}N_2$: C, 79.56; H, 6.16; N, 14.27. Found: C, 79.8; H, 6.3; N, 14.0.

3.1.3. 4-(4-Formylphenylethynyl)-1-methyl-1*H*-pyrazole-3,5-dicarboxylic acid dimethyl ester (2f). The compound was prepared according to the procedure described in Ref. 21 with some modification. Copper(I) iodide (0.05 g, 0.26 mmol) was added to a stirred solution of 4-ethynylbenzaldehyde (2.65 g, 20.4 mmol), 4-iodo-1-methyl-1*H*-pyrazole-3,5-dicarboxylic acid dimethyl ester (**3**) (6.52 g, 20 mmol), palladium(II) chloride (0.1 g, 0.56 mmol), triphenylphosphine (0.25 g, 0.95 mmol) and triethylamine (5 ml) in benzene (50 ml) under an argon atmosphere. The mixture was stirred at 60–70°C for 6 h and then filtered through silica gel. The solvent was distilled off in vacuo and the residue crystallized from ethyl acetate to afford compound **2f** (4.43 g, 68%) as a yellow powder, decomp. at ~190°C; IR: ν_{max}=1485, 1602, 1710, 1735, 2240, 2861, 2957, 3034 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ 3.88 (s, 3H, 3-$COOCH_3$), 3.96 (s, 3H, 5-$COOCH_3$), 4.23 (s, 3H, N–CH_3), 7.74 (d, 2H, *J*=9 Hz, H^2 and H^6), 7.98 (d, 2H, *J*=9 Hz, H^3 and H^5), 10.07 (s, 1H, CHO). Anal. Calcd for $C_{17}H_{14}N_2O_5$: C, 62.57; H, 4.32; N, 8.59. Found: C, 62.8; H, 4.4; N, 8.3.

3.1.4. 4-(6-Methyl-pyridin-3-ylethynyl)-benzaldehyde (5a). By the foregoing palladium-catalyzed procedure, coupling of 5-ethynyl-2-methylpyridine (2.57 g, 22.0 mmol) and 4-bromobenzaldehyde (3.72 g, 20.1 mmol) for 30 min, and column chromatography on silica gel (chloroform) gave alkynylpyridine **5a** (4.27 g, 96%) as a yellowish crystalline solid, mp 146.5–147°C (tetrachloromethane); IR: ν_{max}=1702, 2214 cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.32 (s, 3H, CH_3), 6.48 (d, 2H, *J*=8.5 Hz, H^2 and H^6), 7.26–8.39 (m, 4H, aromatic H), 8.86 (s, 1H, $H^{2'}$), 9.54 (s, 1H, CHO). Anal. Calcd for $C_{15}H_{11}NO$: 81.42; H, 5.01; N, 6.36. Found: C, 81.6; H, 4.9; N, 6.3.

3.1.5. 2-(1*H*-Pyrazol-4-yl)-1-phenylethan-1,2-dione (3c). A mixture of the alkynylpyrazole **2c** (365 mg, 2.17 mmol) and palladium(II) chloride (36 mg, 0.2 mmol) in DMSO (6 ml) was stirred at 120–125°C for 7 h, then cooled, diluted with water (30 ml), and extracted with ethyl acetate (3×30 ml). The combined organic extracts were washed with water (30 ml), brine (30 ml), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a silica gel column (hexane–ethylacetate 1:1, v/v) followed by crystallization from benzene–hexane (1:1, v/v) to afford dione **3c** (373 mg, 86%) as yellow needles, mp 95–96°C; IR: ν_{max}=1447, 1514, 1596, 1652, 1687, 2879, 3037, 3097, 3118, 3175 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.30 (br.s, 1H, pyrazole-H^3), 7.56 (t, 2H, *J*=9 Hz, phenyl-H^3 and H^5), 7.68 (t, 1H, *J*=9 Hz, phenyl-H^4), 8.11 (d, 2?, *J*=9 Hz, phenyl-H^2 and H^6), 8.30 (br.s, 1?, pyrazole-H^5); ^{1}H NMR (DMSO-d_6) δ 7.63 (t, 2H, *J*=9 Hz, phenyl-H^3 and H^5), 7.78 (t, 1H,

J=9 Hz, phenyl-H^4), 7.94 (d, 2?, J=9 Hz, phenyl-H^2 and H^6), 8.12 (br.s, 1H, pyrazole-H^3), 8.57 (br.s, 1H, pyrazole-H^5). Anal. Calcd for $C_{11}H_8N_2O_2$: C, 65.99; H, 4.03; N, 13.99. Found: C, 65.9; H, 4.0; N, 14.0.

3.1.6. 1-(4-Nitrophenyl)-2-(1*H*-pyrazol-4-yl)-ethan-1,2-dione (3d).

A mixture of 4-(4-nitrophenylethynyl)pyrazole (**2d**) (337 mg, 1.58 mmol) and palladium(II) chloride (30 mg, 0.17 mmol) in DMSO (8 ml) was stirred at 135–140°C for 7 h. Workup as for the foregoing 1,2-diketone **3c** gave dione **3d** (283 mg, 73%) as yellow needles, mp 150–151°C (ethanol); IR: ν_{max}=1493, 1533, 1603, 1650, 1671, 3116 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.30 (br.s, 2?, pyrazole-H^3 and H^5), 8.28 (d, 2H, J=9 Hz, phenyl-H^2 and H^6), 8.46 (d, 2H, J=9 Hz, phenyl-H^3 and H^5); ^1H NMR (DMSO-d_6) δ 7.39 (br.s, 2?, pyrazole-H^3 and H^5), 8.13 (d, 2H, J=9 Hz, phenyl-H^2 and H^6), 8.37 (d, 2H, J=9 Hz, phenyl-H^3 and H^5). Anal. Calcd for $C_{11}H_7N_3O_4$: C, 53.88; H, 2.88; N, 17.14. Found: C, 53.7; H, 2.8; N, 17.1.

Alkynes **2a**, **2b**, **2e**, **7a** and **7b** were oxidized in exactly the same manner as **2c**. Alkynes **2f** and **6** were not oxidized under the foregoing conditions while oxidation of alkynes **5a**, **5b** and **9** gave a complex mixture of products.

3.1.7. 1-Phenyl-2-(1,3,5-trimethyl-1*H*-pyrazol-4-yl)-ethan-1,2-dione (3a).

Yield 82%. Yellowish oil; ^1H NMR (CD_2Cl_2) δ 2.16 (s, 3H, pyrazole-3-CH_3), 2.42 (s, 3H, pyrazole-5-CH_3), 3.72 (s, 3H, N–CH_3), 7.51 (t, 2H, J= 9 Hz, phenyl-H^3 and H^5), 7.69 (t, 1H, J=9 Hz, phenyl-H^4), 7.51 (d, 2H, J=9 Hz, phenyl-H^2 and H^6). Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found C, 69.3; H, 5.9; N, 11.4.

3.1.8. 1-(1,5-Dimethyl-1*H*-pyrazol-4-yl)-2-phenylethan-1,2-dione (3b).

Yield 74%. Yellowish powder with mp 89–89.5°C (benzene–hexane); IR: ν_{max}=1459, 1489, 1542, 1597, 1654, 1672, 3061, 3130 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.23 (s, 3H, 5-CH_3), 3.87 (s, 3H, N–CH_3), 7.58 (t, 2H, J=9 Hz, H^3, H^5), 7.72 (t, 1H, J=9 Hz, H^4), 7.89 (d, 2H, J=9 Hz, H^2, H^6), 8.32 (s, 1H, pyrazole-H^5). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.5; H, 5.4; N, 12.1.

3.1.9. 1-(3-Amino-1-methyl-1*H*-pyrazol-4-yl)-2-(4-methoxyphenyl)-ethan-1,2-dione (3e).

Yield 42%. Yellow powder with mp 172–173°C (benzene); IR: ν_{max}=1513, 1574, 1602, 1652, 2846, 2938, 3013, 3194, 3281, 3437 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.64 (s, 3H, N–CH_3), 3.88 (s, 3H, O–CH_3), 6.00 (br. s, 2H, NH_2), 7.13 (d, 2H, J=9 Hz, H^3, H^5), 7.90 (d, 2H, J=9 Hz, H^2, H^6), 7.97 (s, 1H, pyrazole-H^5). Anal. Calcd for $C_{13}H_{13}N_3O_3$: C, 60.22; H, 5.05; N, 16.21. Found: C, 60.4; H, 5.3; N, 16.1.

3.1.10. 1-(4-Methoxy-phenyl)-2-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecen-2-yl)-ethane-1,2-dione (8a).

Yield 79%. Colorless powder, mp 104–104.5°C (benzene); IR: ν_{max}=1424, 1461, 1511, 1572, 1598, 1662 cm^{-1}; ^1H NMR (DMSO-d_6) δ 3.57–3.67 (m, 12H), 3.74–3.83 (m, 4H, $(CH_2CH_2O)_2Ar$), 3.87 (s, 3H, CH_3), 4.08–4.20 (m, 4H, $(CH_2O)_2Ar$), 7.04–7.19 (m, 3H, $H^{2'}$, $H^{6'}$, H^{20}), 7.34 (d, 1H, J=9 Hz, H^{19}), 7.51 (s, 1H, H^3), 7.86 (d, J=9 Hz, 2H, $H^{3'}$, $H^{5'}$). Anal. Calcd for $C_{23}H_{26}O_8$: C, 64.18; H, 6.09. Found: C, 64.4; H, 6.1.

3.1.11. 1-Biphenyl-4-yl-2-(6,7,9,10,12,13,15,16-octahydro-5,8,11,14,17-pentaoxa-benzocyclopentadecen-2-yl)-ethane-1,2-dione (8b).

Yield 84%. Colorless powder with mp 123–124°C (benzene); ^1H NMR (DMSO-d_6) δ 3.57–3.67 (m, 8H, $(CH_2CH_2)_2$), 3.74–3.83 (m, 4H, $(CH_2CH_2O)_2Ar$), 4.11–4.20 (m, 4 H, $(CH_2O)_2Ar$), 7.12 (d, J=9 Hz, 1H), 7.37–7.66 (m, 5H), 7.72–7.84 (m, 2H), 7.91 (d, J=9 Hz, 2H, $H^{3'}$, $H^{5'}$), 7.97 (d, J=9 Hz, 2H, $H^{2'}$, $H^{6'}$). Anal. Calcd for $C_{28}H_{28}O_7$: C, 70.57; H, 5.92. Found: C, 70.5; H, 5.8.

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