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An efficient synthesis of pyrano [4,5-*c*] pyrrole derivatives through microwave—accelerated intramolecular Knoevenagal hetero Diels–Alder reaction

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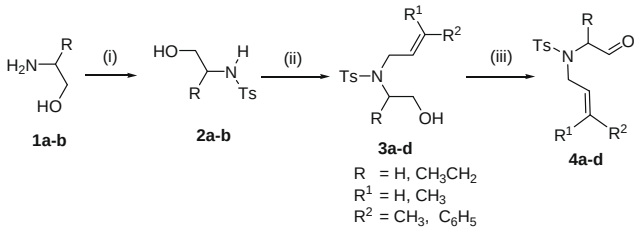
ABSTRACT

Synthesis of novel pyranopyrrole derivatives has been achieved by a one-pot IMHDA reaction of N-substituted aldehydes with various diones in the presence of ethylene diaminediacetate (EDDA) in excellent yields under mild conditions.

The intramolecular Diels–Alder reaction is a widely used method for the synthesis of six-membered heterocyclic compounds.[1a–e] Many heterocycles such as quinolines, pyrroles, and pyrans have received enormous attention from synthetic chemists from the standpoint of both their preparation and their reactivity. The synthesis of pyran and its hydrogenated form has gained importance, since many natural products such as carbohydrates, talaromycines, milbemycines, avermectins, pheromones, and iridoids contain pyran skeleton[2a–e] and possess interesting biological activities with potential medical applications.[3a,b] The domino hetero Diels–Alder reaction is one of the most important methods for the construction of heterocyclic compounds.[4a–h] In the present work, we propose to utilize hetero Diels–Alder reaction as a tool for the construction of pyranopyrroles which are structurally related to natural products. Symmetrical 1,3-diones as heterodienes have been subjected to intramolecular cycloaddition reaction for the synthesis of complex polycyclic heterocycles.[5] A number of reports are available for the synthesis of pyrans and their benzopyran analogues but there is no literature available on pyranopyrrole derivatives.[6a–f]

In the course of our investigation directed toward the synthesis of pyrrole derivatives, herein we report a precise and new route for the synthesis of pyranopyrrole derivatives based on tandem Knoevenagel HDA reaction. Domino hetero Diels–Alder reaction has been well exploited by Tietze for the synthesis of polycyclic compounds.[7a,b] In our present study, we have used *N*-alkenyl aldehyde for the first time in an intramolecular hetero Diels–Alder reaction for the synthesis of pyranopyrrole derivatives in a stereoselective manner.

The strategy we have developed begins with the reaction of cyclic 1,3-dicarbonyl compounds and *N*-alkenyl aldehydes in the presence of EDDA in toluene. The required substrates for hetero Diels–Alder reaction were prepared in three steps from commercially available starting materials. In the first step, sulfonylation of ethanolamines **1a–b** with tosyl chloride under standard PTC reaction conditions proceeded well to provide the sulfonamide derivatives **2a–b**. N-Alkylation of sulfonamides **2a–b** with prenyl bromide/cinnamyl bromide in the presence of potassium carbonate yielded *N*-tosyl-*N*-prenyl/cinnamyl-aminoethanols **3a–d** which on oxidation with IBX in DMSO afforded the required *N*-alkenyl aldehydes **4a–d** in good yield (98%) (Scheme 1).



Scheme 1. Synthesis of *N*-alkenyl aldehydes. Reagents and conditions: (i) TBAB, 10% NaOH/benzene, tosyl chloride, 0 °C–rt; 8 h, 90%; (ii) prenyl/cinnamyl bromide K_2CO_3/acetone, 12 h, 90%; (iii) iodoxybenzoic acid, DMSO, 2–2.5 h, 98%.

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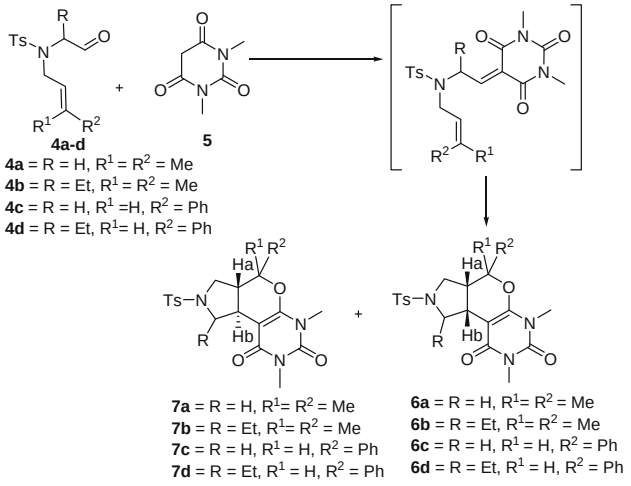


Scheme 2. Synthesis of pyranopyrroles through IMKHDA reaction. Reagents and conditions: Method A: EDDA, toluene, reflux; Method B: toluene, MW.

The alkenyl aldehydes so obtained were reacted with 1,3-diones under suitable reaction conditions to achieve the synthesis of pyranopyrrole ring systems through intramolecular Knoevenagel hetero Diels–Alder reaction. Thus, the reaction of alkenyl aldehyde **4a** with barbituric acid **5** in the presence of EDDA in reflux in toluene proceeded through intramolecular Knoevenagel HDA pathway to afford a mixture of pyranopyrrole **6a** and **7a** (35:65) with an overall yield of 62%. The products were separated by column chromatography and the structures were assigned on the basis of spectroscopic studies. The ^{1}H NMR spectrum of compound **6a** exhibited two singlets at δ 1.22 and 1.49 for geminal

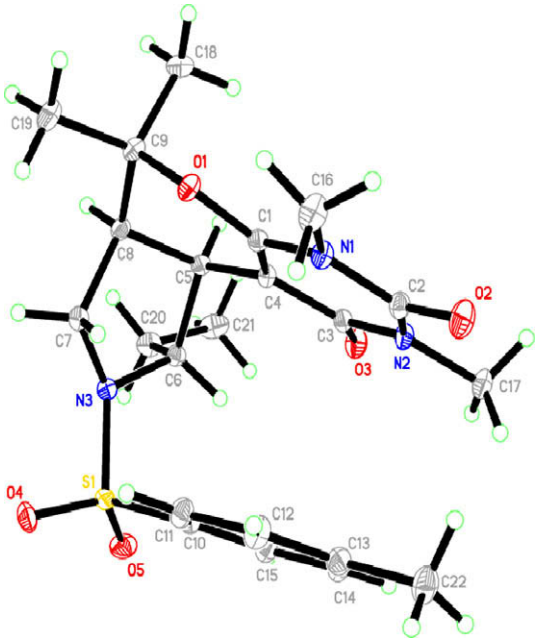
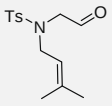
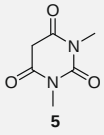
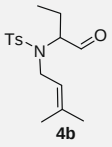
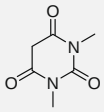
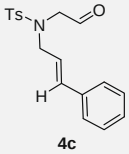
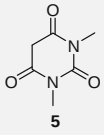
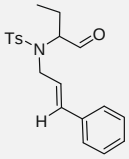
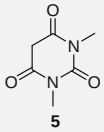


Figure 1. ORTEP diagram of **6b**.

dimethyl protons, a singlet at δ 2.42 for the aromatic methyl, and two singlets at δ 3.27and 3.28 for *N*-CH_3 protons of the pyrimidine ring. The *N*-CH_2 protons of the pyrrolidine ring were observed as multiplets in 2.96–3.04 (2H) and two doublet of doublets at δ 3.58 (J = 9.0, 9.0, 1H) and δ 4.36 (J = 6.0, 9.0, 1H). Particularly diagnostic were the protons Ha and Hb situated at the ring

Table 1
Reaction times and yields of the domino reactions of **4a–d** with **5** under various conditions

Entry	Aldehydes	1,3-Diones	Conditions	Ratio of the products			
				Time	Cis	Trans	Overall yield (%)
1	 **4a**	 **5**	Method A Method B	6 h 2 min	35 30	65 70	62 74
2	 **4b**	 **5**	Method A Method B	6 h 2 min	20 15	80 85	67 80
3	 **4c**	 **5**	Method A Method B	6 h 2 min	35 30	65 70	60 72
4	 **4d**	 **5**	Method A Method B	6 h 2 min	33 25	67 75	63 75

Reaction conditions: Method A: toluene, reflux; Method B: toluene, MW.

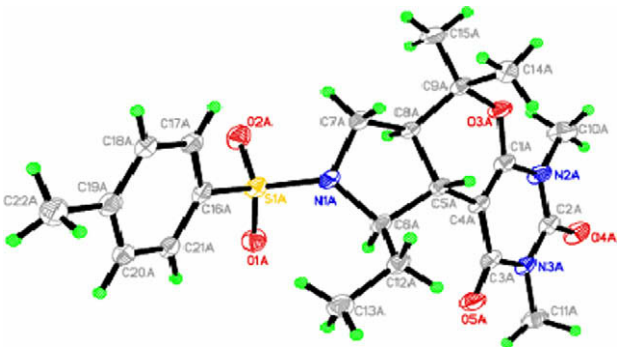


Figure 2. ORTEP diagram of **7b**.

junctions showing doublets of triplets at δ 1.89 (J = 6.0, 12.0) and δ 2.48 (J = 6.0, 12.0), respectively. On the other hand, the ^{1}H NMR spectrum of **7a** exhibited one doublet of triplet at δ 2.59 (J = 9.0, 9.0) and one multiplet at δ 2.96–3.04 for Ha and Hb protons, respectively. The low value of the coupling constant (6 Hz) between Ha and Hb in **6a** indicated the cis fusion at the ring junctions. Similar type of δ values were observed for trans product **7a**, but the trans fusion at the ring junction was discerned by the high coupling constant value (9 Hz).

To improve the reaction yields and chemoselectivity, we carried out the reaction under microwave conditions.[8a–f] We were pleased to find that the reaction in toluene under microwave irradiation without base worked well to provide adducts **6a** and **7a** (30:70) with an overall yield of 74%. Thus, there was an increase in the

Table 2
Reaction times and yields of the domino reactions of **4a–d** with various symmetrical 1,3-diones under various conditions

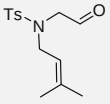
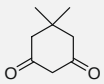
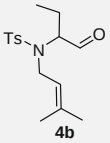
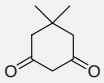
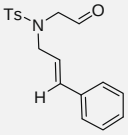
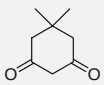
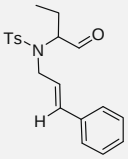
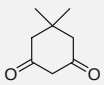
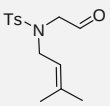
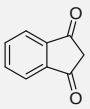
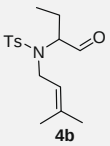
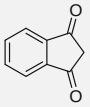
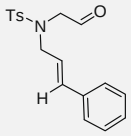
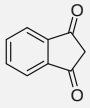
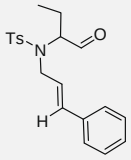
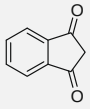
Entry	Aldehydes	1,3-Diones	Conditions	Ratio of the products			
				Time	Cis	Trans	Overall yield (%)
1	 **4a**	 **8**	Method A Method B	6 h 2 min	31 30	69 70	63 75
2	 **4b**	 **8**	Method A Method B	6 h 2 min	25 20	75 80	66 80
3	 **4c**	 **8**	Method A Method B	6 h 2 min	23 15	77 80	60 77
4	 **4d**	 **8**	Method A Method B	6 h 2 min	19 15	81 85	64 81
5	 **4a**	 **11**	Method A Method B	8 h 2.5 min	18 15	80 85	57 68
6	 **4b**	 **11**	Method A Method B	8 h 2 min	17 15	83 85	60 75

Table 2 (*continued*)

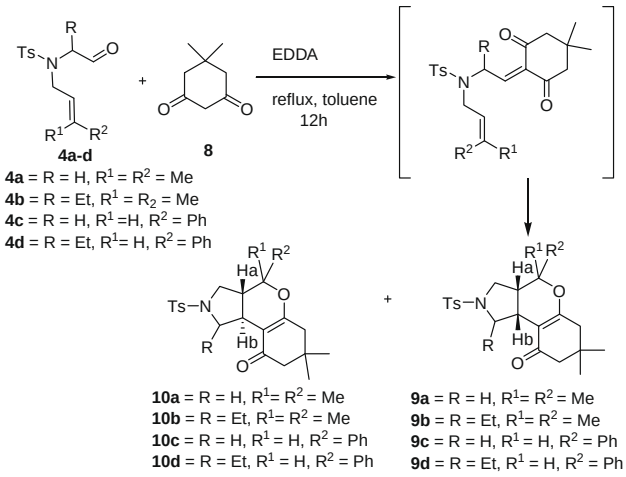
Entry	Aldehydes	1,3-Diones	Conditions	Ratio of the products			
				Time	Cis	Trans	Overall yield (%)
7	 **4c**	 **11**	Method A Method B	8 h 2.5 min	12 10	88 90	58 68
8	 **4d**	 **11**	Method A Method B	8 h 2.5 min	15 11	85 89	63 72

Reaction conditions: Method A: toluene, reflux; Method B: toluene, MW.

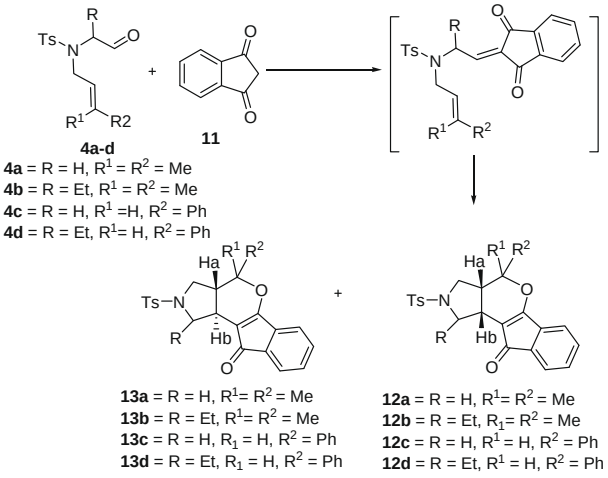
chemical yield with a slight improvement in the chemoselectivity. Encouraged by these findings, we expanded the scope of the hetero Diels–Alder reaction by changing the alkenyl substituent of the internal dipolarophile. Thus, the reaction of **4b** with barbituric acid **5** (Scheme 2) was tested under optimized reaction conditions and the results are summarized in Table 1. The substrate **4b** also reacted in the same way as **4a**, but gave better yield of the product in shorter duration of time. These results show the efficiency of the prenyl-substituted dienophile.

Having optimized the reaction conditions for the stereoselective synthesis of pyrano[4,5-*c*]pyrrole derivatives, we conducted the intramolecular Knoevenagel hetero Diels–Alder reaction by employing various symmetrical diones, namely dimedone and indane-1,3-dione with aldehydes **4a–d** (Schemes 3 and 4). The results are summarized in Table 2. The intramolecular Knoevenagel hetero Diels–Alder reaction of **4a–d** with indane-1,3-dione in refluxing toluene completed in 6 h (Scheme 4). As observed in the former case, we readily isolated the expected *cis* and *trans* pyrano[4,5-*c*]pyrrole derivatives simply by changing from toluene/reflux conditions to microwave irradiation.[9]

The structures of the cis and trans products were determined on the basis of detailed 2D NMR studies. The structures of the cycloadducts were further unambiguously supported by the single crystal



Scheme 3. Synthesis of pyranopyrroles through IMKHDA reaction. Reagents and conditions: Method A: toluene, reflux; Method B: toluene, MW.



Scheme 4. Synthesis of pyranopyrroles through IMKHDA reaction. Reagents and conditions: Method A: toluene, reflux; Method B: toluene, MW.

X-ray diffraction analysis of some of the products (see Figs. 1 and 2).[10a,b] Similarly, the protocol was extended further to other 1,3-diones and alkenyl aldehydes **4a**–**d** to form a series of pyranopyrroles in moderate to good yields.

In conclusion, we have synthesized cis and trans isomers of the pyranopyrrole derivatives through intramolecular domino Knoevenagel hetero Diels–Alder reaction. The preceding studies demonstrate the scope of the intramolecular Knoevenagel hetero Diels–Alder reaction for the synthesis of *cis* and *trans* pyrrolo pyrrole products. We have shown that use of microwave irradiation improves the overall yield of the products as well as stereoselectivity.

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9. *General procedure for the intramolecular domino Knoevenagel hetero Diels–Alder reaction*: Method A: To a solution of 4-hydroxyquinolinone (1 mmol) in toluene the corresponding 2(*N*-prenyl-*N*-tosylamino)acetaldehyde (1 mmol) and the base EDDA (1 mmol) were added and the reaction mixture was refluxed, till the completion of the reaction. The solvent was then evaporated under reduced pressure and the residue was subjected to column chromatography using hexane–ethyl acetate (7.5:2.5) mixture.
   Method B: A solution of 1,3-diones (1 mmol) and the corresponding aldehyde (1 mmol) in toluene (2 ml) without base was irradiated with microwave (MODEL = Chem Discover benchmate microwave 300 W, $P = 100$, $T = 110$ °C, 20 MHz) until the TLC showed the disappearance of the starting material. After removal of the solvent, the crude reaction mixture was subjected to column chromatography using hexane–ethyl acetate (7.5:2.5) mixture.
   Representative spectral data of the products; Compound **6a**: white solid; mp: 180–182 °C; IR (KBr): 1695.3, 1637.4, 1340.4, 1159.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.22 (s, 3H),1.49 (s, 3H), 1.89 (dt, H_a, $J = 6.0$, 12.0 Hz), 2.42 (s, 3H), 2.48 (dt, H_a, $J = 6.0$, 12.0 Hz), 2.96–3.04 (m, 2H), 3.27 (s, 3H), 3.28 (s, 3H), 3.58 (dd, 1H, $J = 9.0$, 9.0 Hz), 4.36 (dd, 1H, $J = 6.0$, 9.0 Hz), 7.33 (d, 2H, $J = 9.0$ Hz), 7.40 (d, 2H $J = 6.0$ Hz); ^{13}C NMR: 20.67, 21.49, 27.70, 28.16, 28.96, 33.81, 47.63, 49.65, 52.20, 83.87, 86.54, 127.26, 129.82, 134.54, 143.57, 150.97, 155.79, 161.92. MS *m/z*: 419.79 (M^+); Anal. Calcd for $C_{20}H_{25}N_3O_5S$: C, 57.19; H, 6.97; N, 9.98. Found: C, 57.31; H, 6.12; N, 10.10.
   Compound **7a**: white solid; mp: 160–162 °C; IR (KBr): 1695.3, 1647.1, 1342.4,1159.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 3H), 1.41 (s, 3H), 2.40 (s, 3H), 2.59 (dt, H_a, $J = 9.0$, 9.0 Hz), 2.96–3.04 (m, 2H), 3.14 (s, 3H), 3.20 (s, 3H), 3.58–3.65 (m, 2H), 3.98 (d, 1H, $J = 12.0$ Hz), 7.17 (d, 2H, $J = 9.0$ Hz), 7.57 (d, 2H $J = 9.0$ Hz); ^{13}C NMR: 21.57, 25.02, 26.25, 27.61, 28.13, 30.87, 32.68, 45.21, 47.34, 51.74, 80.45, 85.07, 127.26, 128.91, 133.57, 143.73, 150.42, 154.18, 162.21. MS *m/z*: 419.86 (M^+); Anal. Calcd for $C_{20}H_{25}N_3O_5S$: C, 57.28; H, 6.00; N, 10.02. Found: C, 57.12; H, 6.11; N, 10.18.
   Compound **9a**: white solid; mp: 146–148 °C; IR (KBr): 1619.4, 1334.7, 1155.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.01 (s, 6H), 1.09 (s, 3H), 1.36 (s, 3H), 1.78 (dt, H_a, $J = 6.0$, 12.0 Hz), 2.18 (m, 5H), 2.42 (s, 3H), 2.89 (m, H, H_b), 3.51 (dd, 1H, $J = 6.0$, 9.0 Hz),4.33 (dd, 1H, $J = 6.0$, 12.0 Hz), 7.31 (m, 2H), 7.73 (d, 2H $J = 6.0$ Hz); ^{13}C NMR: 20.54, 21.51, 27.90, 28.28, 28.59, 32.04, 33.67, 42.44, 47.56, 49.75, 50.45, 52.09, 80.07, 109.75, 127.26, 129.74, 134.82, 143.34, 169.66, 196.66. MS *m/z*: 403.32 (M^+);Anal. Calcd for $C_{22}H_{29}NO_4S$: C, 65.32; H, 7.21; N, 3.42. Found: C, 65.45; H, 7.10; N, 3.50.
   Compound **10a**: white solid; mp: 199–201 °C; IR (KBr): 1612.2, 1334.6, 1159.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.736 (s, 3H), 0.94 (s, 3H), 1.17 (s,3H), 1.29 (s, 3H), 1.87–2.11 (m, 4H), 2.39–245 (m, 1H), 240 (s, 3H), 2.87 (t, 1H, $J = 9.0$ Hz), 2.98 (t,1H, $J = 6.0$), 3.37–3.41 (distorted dt, 1H, $J = 3.0$, 12.0 Hz), 3.50–3.64 (m, 2H), 7.28 (d, 2H, $J = 6.0$ Hz), 7.65 (d, 2H $J = 6.0$ Hz); ^{13}C NMR: 21.47, 25.17, 26.36, 27.56, 28.30, 31.80, 31.86, 42.67, 45.30, 47.46, 50.70, 52.30, 80.05, 109.27, 127.65, 129.61, 134.65, 143.15, 168.53, 197.48. MS *m/z*: 403.92 (M^+); Anal. Calcd for $C_{22}H_{29}NO_4S$: C, 65.41; H, 7.16; N, 3.37. Found: C, 65.52; H, 7.26; N, 3.52.
   Compound **12a**: white solid; mp: 149–151 °C; IR (KBr): 1721.1, 1335.7, 1158.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.24 (s, 3H), 1.52 (s, 3H), 1.80 (dt, H_a, $J = 9.0$, 12.0 Hz), 2.28–2.38 (m, 1Hb), 2.95–3.05 (m, 2H), 3.57 (dd, H_a, $J = 6.0$, 12.0 Hz), 4.17 (dd, 1H, $J = 6.0$, 12.0 Hz), 7.07–7.76 (m, 8ArH); ^{13}C NMR: 20.64, 21.50, 27.98, 33.05, 47.64, 50.63, 50.70, 83.57, 106.47, 118.13, 121.14, 127.30, 129.84, 130.31, 131.88, 133.10, 134.66, 137.44, 143.61, 174.06. MS *m/z*: 409.43 (M^+); Anal. Calcd for $C_{23}H_{23}NO_4S$: C, 67.31; H, 5.68; N, 3.28. Found: C, 67.43; H, 5.51; N, 3.39.
   Compound **13a**: white solid; mp: 171–173 °C; IR (KBr): 169.3, 1334.7, 1159.1 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.46 (s, 3H), 2.00 (s, 3H), 2.52 (dt, H_a, $J = 6.0$, 12.0 Hz), 2.90 (t, 1H, $J = 12.0$), 2.97 (t, 2H, $J = 6.0$ Hz), 3.55–3.64 (m, 2H), 3.57 (d, 1H, $J = 12.0$ Hz), 6.91–7.53(m, 8ArH); ^{13}C NMR: 21.42, 25.83, 26.44, 31.13, 45.95, 46.79, 50.74, 80.63, 106.54, 117.72, 120.74, 127.16, 129.32, 129.99, 131.78, 133.28, 137.41, 143.46, 172.61. MS *m/z*: 409.36 (M^+); Anal. Calcd for $C_{23}H_{23}NO_4S$: C, 67.49; H, 5.51; N, 3.45. Found: C, 67.60; H, 5.62; N, 3.59.
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