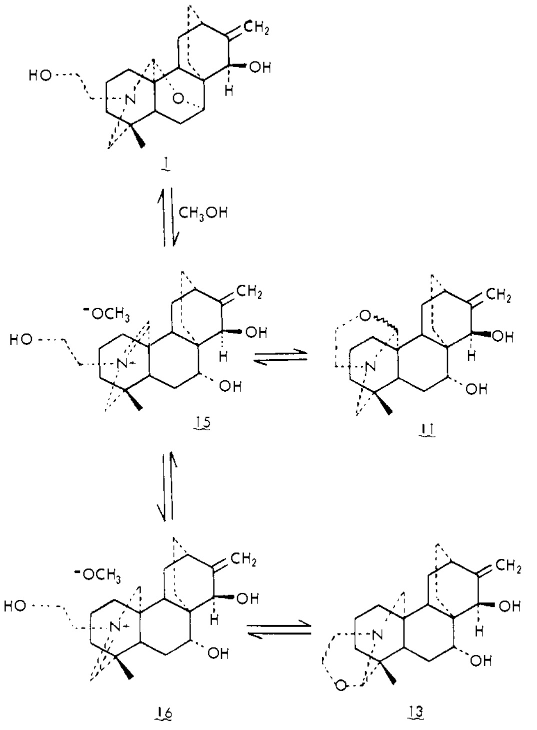
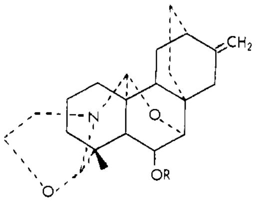
deuterated methanol under a nitrogen atmosphere, a mixture of C(19),(20)-deuterated ajaconine and C(19),(20)-deuterated 7α-hydroxyisoatisine was formed. This deuteration experiment indicates that ajaconine ionizes and rearranges to 7α-hydroxyisoatisine (**13**) and that these two species are in equilibrium in refluxing methanol. The mechanism for the rearrangement may now be considered.

The species **15** closes to ajaconine (**1**) and not to **11** because the closure **15** → **11**, being partially disfavored, is much slower than the closure **15** → **1**. However, the species **15** should undergo an isomerization (**15** → **16**) which has a precedent in the veatchine → garryine and the atisine (**3**) → isoatisine (**4**) isomerization. The species **16** should readily close now to the oxazolidine (**13**), in spite of the closure being *partially disfavored because there is no faster process in competition with this ring closure.*



The rearrangement of ajaconine (**1**) into 7α-hydroxyisoatisine (**13**) represents an unusual example of a Baldwin rule "disfavored" 5-endo-trig-ring closure. On the basis of the above results we conclude that the ether linkage of ajaconine ionizes in ionic solvents and that ajaconine rearranges via a disfavored 5-endo-trig process to an isooxazolidine ring containing compound.

Because of the unusual character of the C(7)-C(20) ether system in ajaconine, it would be interesting to examine the behavior of the spiradine-type alkaloids (**17**, **18**)[12] in ionic solvents to determine what rearrangement products are formed and to see which ether linkage forms an immonium salt.



17 R = Ac Spiradine F

18 R = H Spiradine G

Acknowledgment. We acknowledge the contributions of Professor K. Wiesner to this paper. His referee's report provided an interpretation of the behavior of the internal carbinolamine ethers which we have adopted in the revision of this paper. We thank Mr. Howard C. Higman of the Tobacco and Health Laboratory, USDA-ARS, Richard Russell Research Center, Athens, Ga. for the mass spectrum and Dr. Rajinder Sawhney for isolation of a sample of ajaconine.

References and Notes

(1) Dvornik, D.; Edwards, O. E. *Proc. Chem. Soc.* **1958**, 305.
(2) Dvornik, D.; Edwards, O. E. *Tetrahedron* **1961**, *14*, 54 and references cited therein.
(3) Pelletier, S. W. *J. Am. Chem. Soc.* **1965**, *87*, 799.
(4) Pelletier, S. W.; Keith, L. H. "The Alkaloids", R. H. F. Manske Ed., Academic Press: New York, **1970**; Vol. 12, Chapter 2, and references cited therein.
(5) The authors did not report the identification of any product in this mixture.
(6) Wiesner, K.; Edwards, J. A. *Experientia* **1955**, *11*, 255. Pelletier, S. W.; Jacobs, W. A. *Chem. Ind. (London)* **1955**, 1385. Pelletier, S. W.; Mody, N. V. *Tetrahedron Lett.* **1977**, 1477.
(7) The ^{13}C NMR spectrum of ajaconine hydrochloride in D_2O was compared with the spectrum of atisinium chloride to confirm its structure as **10**.
(8) These downfield shifts do not result from ordinary solvent effects; e.g., examination of dihydroajaconine shows essentially the same chemical shifts in either CD_3OD or $CDCl_3$.
(9) In a typical experiment, 100 mg of ajaconine in 10 mL of CH_3OH was refluxed over a steam bath for 1.5 h to achieve 60% rearranged product **13**. The rate of conversion depends upon the concentration.
(10) Pelletier, S. W.; Mody, N. V. *J. Am. Chem. Soc.* **1977**, *99*, 284. Mody, N. V.; Pelletier, S. W. *Tetrahedron* **1978**, *34*, 2421.
(11) Pelletier, S. W.; Oeltmann, T. N. *Tetrahedron* **1968**, *24*, 2019.
(12) Toda, M.; Hirata, Y. *Tetrahedron Lett.* **1968**, 5565.

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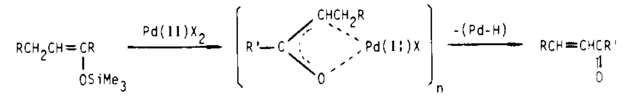
Received June 19, 1978

Cyclization Reactions via Oxo-π-allylpalladium(II) Intermediates

Sir:

In the previous paper[1] we reported Pd(II) assisted dehydrosilylation[2] of silyl enol ethers leading to α,β-unsaturated carbonyl compounds, in which oxo-π-allylpalladium(II) complexes were proposed as key intermediates. In support of the reaction mechanism involving the oxo-π-allylpalladium(II) intermediate, we[3] recently succeeded in the isolation of a stable 2-*tert*-butyl-π-oxopropenylpalladium(II) complex in the reaction of silyl enol ether of pinacolone with $Pd^{II}Cl_2(PhCN)_2$.



Herein, we report Pd(II) promoted intramolecular cyclization of silyl enol ethers (**1**) of alkenyl methyl ketones to produce cyclic α,β-unsaturated ketones (**3**), in which oxo-π-allylpalladium(II) complexes (**2**) may be involved as key intermediates.

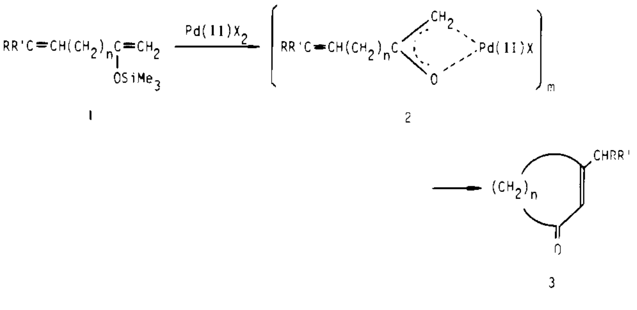


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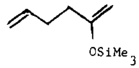
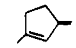
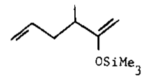
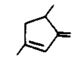
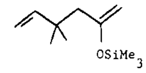
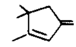
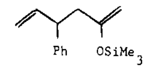
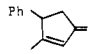
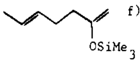
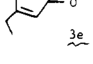
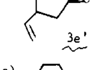
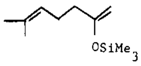
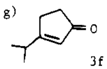
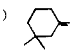
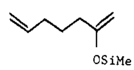
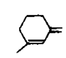
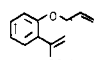
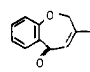
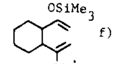
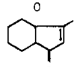
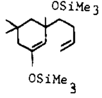
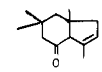
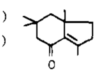
Table I. Pd(II)-Catalyzed Preparation of Cyclic α,β-Unsaturated Ketones[a]

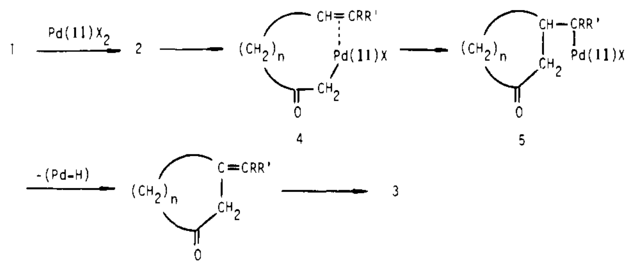
Silyl enol ether	Pd(II) salt (equiv)	Product (%)[b]
 **1a**	$Pd(OAc)_2$ (1)	 **3a** (87)[c]
1a	$Pd(OAc)_2$ (0.5)[d]	**3a** (70)[c]
 **1b**	$Pd(OAc)_2$ (1)	 **3b** (98)[c]
 **1c**	$Pd(OAc)_2$ (1)	 **3c** (~100)[e]
 **1d**	$Pd(OAc)_2$ (1)	 **3d** (83)[e]
[f] **1e**	$Pd(OAc)_2$ (1)	 **3e** (35),[c]  **3e'** (25)[c]
 **1f**	$PdCl_2(PhCN)_2$ (1)[g]	 **3f** (40)[c]  **3f'** (<10)[c]
 **1g**	$Pd(OAc)_2$ (1)	 **3g** (36)[c]
 **1h**	$Pd(OAc)_2$ (1)	 **3h** (25)[e]
[f] **1i**	$Pd(OAc)_2$ (1)	[h] **3i** (99)[e]
 **1j**	$Pd(OAc)_2$ (1)	 **3j** (27)[c],[h]  **3j'** (32)[c]

[a] Cyclization was carried out by using 1 mmol of silyl enol ether and 1 mmol of $Pd(OAc)_2$ in 4 mL of acetonitrile at room temperature for 10 h, unless otherwise stated. [b] The yields are not necessarily optimum since each run was performed only once. [c] Yields, based upon the starting silyl enol ethers are determined by GLC. [d] Plus 0.5 mmol of *p*-benzoquinone was used. [e] Isolated yields. [f] A cis and trans mixture. [g] Use of $Pd(OAc)_2$ gave a trace of **3f**. Benzene (12 mL) was used instead of acetonitrile solvent.

A typical experimental procedure is illustrated in the $Pd^{II}(OAc)_2$ induced cyclization of 2-trimethylsilyloxy-1,5-hexadiene (**1a**) producing 3-methyl-2-cyclopentenone (**3a**). To a stirring solution of 225 mg (1 mmol) of $Pd^{II}(OAc)_2$ in 4 mL of acetonitrile, 170 mg (1 mmol) of 2-trimethylsilyloxy-1,5-hexadiene (**1a**) was dropwise added under nitrogen at room temperature, and then the resultant mixture was stirred for 10 h at room temperature. The reaction progressed with the deposit of metallic palladium. The reaction mixture was condensed under reduced pressure and triturated with hexane. 3-Methyl-2-cyclopentenone (**3a**) was isolated in an 87% yield by preparative GLC; **3a** was identified by comparison of its IR and NMR spectra with those of an authentic sample.

In the above procedure, the amount of $Pd^{II}(OAc)_2$ can be reduced to 0.5 molar equiv in the presence of *p*-benzoquinone, which is a reoxidant[4] to regenerate an active Pd(II) species, although the yield of 3-methyl-2-cyclopentenone (**3a**) was decreased to some extent. Results are summarized in Table I. Similarly, the cyclizations of 2-trimethylsilyloxy-1,5-hexadiene with substituents at 3 and 4 position, such as 2-trimethylsilyloxy-3-methyl-1,5-hexadiene (**1b**), 2-trimethylsilyloxy-4,4-dimethyl-1,5-hexadiene (**1c**), and 2-trimethylsilyloxy-4-phenyl-1,5-hexadiene (**1d**), readily took place producing the corresponding 3-methyl-2-cyclopentenone derivatives (**3**)[5] in fair to excellent yields, but silyl enol ethers **1e** and **1f** with the internal carbon-carbon double bond were cyclized in significantly decreased yields. 2-Trimethylsilyloxy-1,5-heptadiene (**1e**) was converted to a mixture of 3-ethyl-2-cyclopentenone (**3e**, 35% yield) and its isomer, 3-vinylcyclopentanone (**3e'**, 25% yield). 2-Trimethylsilyloxy-6-methyl-1,5-heptadiene (**1f**) was converted into 3-isopropyl-2-cyclopentenone (**3f**, 40% yield) with a small amount of 3,3-dimethylcyclohexanone (**3f'**).[6]

Scheme I



The cyclization with 2-trimethylsilyloxy-1,6-heptadiene (**1g**) afforded six-membered 3-methyl-2-cyclohexenone (**3g**), but in a low yield. Some attempts to prepare larger than seven-membered cyclic ketone by the present method were unsuccessful.[7] However, the silyl enol ether (**1h**) of *o*-(allyloxy)acetophenone, in which both the olefinic group and the silyl enol ether group are geometrically in close proximity to each other, was cyclized to seven-membered 6,7-benzo-3-methyl-5-oxa-2-cycloheptadiene (**6h**)[8] in 25% yield.

The present procedure for cyclization was successfully used for the preparation of 6/5 fused bicyclic ketones. Thus, 1-(1-trimethylsilyloxyvinyl)-2-vinylcyclohexane (**1i**) was cyclized to 6/5 fused bicyclic ketone **3i**[9] in a quantitative yield.

The probable course of the cyclization reaction is shown in Scheme I. The 2-silyloxyalkadiene **1** reacts with $Pd^{II}(OAc)_2$ to produce oxo-π-allylpalladium(II) complex (**2**), which undergoes intramolecular insertion of the olefin resulting in the σ-alkylpalladium(II) complex **5**. On β elimination of hydride palladium species the complex **5** gives cyclic ketone **6**, which may rearrange to the α,β-unsaturated cyclic ketone **3**. It is conceivable that σ-(α-ketomethyl)palladium(II) complex **4**, in which the olefinic group is coordinated on palladium, is formed as a transient species prior to the intramolecular olefin insertion. The intramolecular olefin insertion in the oxo-π-allylpalladium(II) complex **2** occurs probably in a concerted fashion, permitting palladium to bind to the outer carbon atom of the olefin, as indicated by exclusive production of five-membered cyclic ketones rather than six-membered cyclic ketones from **1a–d**. Experimental verification of the mechanism involving oxo-π-allylpalladium(II) intermediates is in progress.[10]

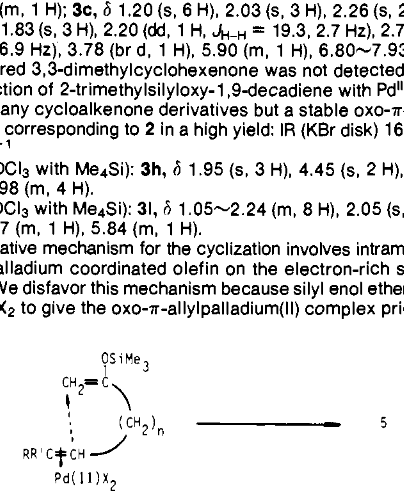
The present reaction is useful especially for the preparation of 3-methyl-2-cyclopentenone derivatives since 2-trimethylsilyloxy-1,5-hexadienes with substituents at the 3 and 4 positions, such as **1a–d** and **1i**, are cyclized to the corresponding 3-methyl-2-cyclopentenone derivatives in high yields under the mild reaction conditions. The starting 2-trimethylsilyloxy-1,5-hexadienes are readily prepared by the Cu(I) catalyzed conjugate addition[11] of vinyl Grignard reagent to various α,β-unsaturated methyl ketones and then treatment of the resulting 3-butenyl methyl ketones with trimethylchlorosilane in the presence of lithium diisopropylamide at −78 °C.[12]

π-Allylpalladium(II) complexes have been widely utilized as versatile synthetic intermediates in organic syntheses.[13] Elegant cyclization reactions with π-allylpalladium(II) intermediates leading to humulene[14a] and macrolide[14b] syntheses were recently reported by Yamamoto and Nozaki and by Trost, respectively. The oxo-π-allylpalladium(II) complex, despite its similarity in structure to the π-allylpalladium(II) complex, has been scarcely investigated because of the lack of a general preparative method of the oxo-π-allylpalladium(II) complex. The present cyclization reaction, which may involve the oxo-π-allylpalladium(II) complex as a key intermediate, is interestingly compared with π-allylpalladium(II) catalyzed synthetic reactions leading to the formation of carbon-carbon bonds.

Synthetic applications of oxo-π-allylpalladium(II) intermediates are now in progress.

References and Notes

(1) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978,** *43*, 1011-1013.
(2) Recently we found a catalytic dehydrosilylation of silyl enol ethers with $Pd^{II}(OAc)_2$ catalyst, in which an active Pd(II) species is regenerated by $Cu^{II}(OAc)_2$ with O_2. For example, to a solution of 23 mg (0.1 mmol) of $Pd^{II}(OAc)_2$ and 36 mg (0.2 mmol) of $Cu^{II}(OAc)_2$ in 8 mL of acetonitrile, 184 mg (1 mmol) of 6-methyl-1-trimethylsilyloxy-1-cyclohexene was added with stirring at room temperature, and then the resultant solution was stirred by bubbling oxygen through the solution for 24 h. Gas chromatography of the reaction mixture indicated that 6-methyl-2-cyclohexenone was produced in a quantitative yield.
(3) Ito, Y.; Hirao, T.; Saegusa, T. unpublished work.
(4) Use of $Cu^{II}(OAc)_2$ in combination with O_2 as a reoxidant in the present cyclization did not give any successful results.
(5) NMR (CCl_4 with Me_4Si): **3b,** δ 1.10 (d, 3 H), 2.10 (s, 3 H), 1.73~3.00 (m, 3 H), 5.58 (m, 1 H); **3c,** δ 1.20 (s, 6 H), 2.03 (s, 3 H), 2.26 (s, 2 H), 5.73 (m, 1 H); **3d,** δ 1.83 (s, 3 H), 2.20 (dd, 1 H, J_{H-H} = 19.3, 2.7 Hz), 2.79 (dd, 1 H, J_{H-H} = 19.3, 6.9 Hz), 3.78 (br d, 1 H), 5.90 (m, 1 H), 6.80~7.93 (m, 5 H).
(6) The desired 3,3-dimethylcyclohexenone was not detected.
(7) The reaction of 2-trimethylsilyloxy-1,9-decadiene with $Pd^{II}Cl_2(PhCN)_2$ did not give any cycloalkenone derivatives but a stable oxo-π-allylpalladium complex corresponding to **2** in a high yield: IR (KBr disk) 1655, 1520, 990, 910 cm^{-1}
(8) NMR ($CDCl_3$ with Me_4Si): **3h,** δ 1.95 (s, 3 H), 4.45 (s, 2 H), 6.08 (m, 1 H), 6.58~7.98 (m, 4 H).
(9) NMR ($CDCl_3$ with Me_4Si): **3l,** δ 1.05~2.24 (m, 8 H), 2.05 (s, 3 H), 2.48 (m, 1 H), 2.77 (m, 1 H), 5.84 (m, 1 H).
(10) An alternative mechanism for the cyclization involves intramolecular attack of the palladium coordinated olefin on the electron-rich silyl enolate as shown. We disfavor this mechanism because silyl enol ether rapidly reacts with $Pd^{II}X_2$ to give the oxo-π-allylpalladium(II) complex prior to the cyclization.[7]



(11) House, H. O.; Latham, R. A.; Slater, C. D. *J. Org. Chem.* **1966,** *31*, 2667-2669.
(12) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969,** *34*, 2324-2336.
(13) Maitlis, P. M. "The Organic Chemistry of Palladium", Academic Press: New York, N.Y., Vol. I and II, 1971.
(14) (a) Kitagawa, Y.; Itoh, A.; Hashimoto, S.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1977,** *99*, 3864-3867. (b) Trost, B. M.; Verhoeven, T. R. *ibid.* **1977,** *99*, 3867-3868.

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Received June 5, 1978

Fourier Transform Infrared Vibrational Circular Dichroism

Sir:

We report here the observation of vibrational circular dichroism (VCD) with a Fourier transform infrared (FT IR) spectrometer. The method used to obtain the VCD spectra represents the first demonstration of high-frequency modulated, differential FT IR spectroscopy, the general theory of which has been recently developed.[1] Since the initial discovery[2] and verification[3] of VCD, measurements have been achieved only with dispersive, grating instruments where spectra are generated by scanning a monochromator.[4] Since reported VCD signals are approximately four to five orders of magnitude smaller than the absorbance of the sample, signal-to-noise ratio enhancement using extensive electronic filtering and long scanning times is required. The present observation demonstrates the feasibility of measuring VCD using an FT IR spectrometer system having fundamental advantages over its dispersive counterpart in both signal quality due to increased throughput, Jacquinot's advantage,[5] and reduced measurement time due to spectral multiplexing, Fellgett's advantage.[5] The observation of FT IR-VCD points to a new dimension in VCD spectroscopy which should lead to significant improvements as this method is further developed and optimized.

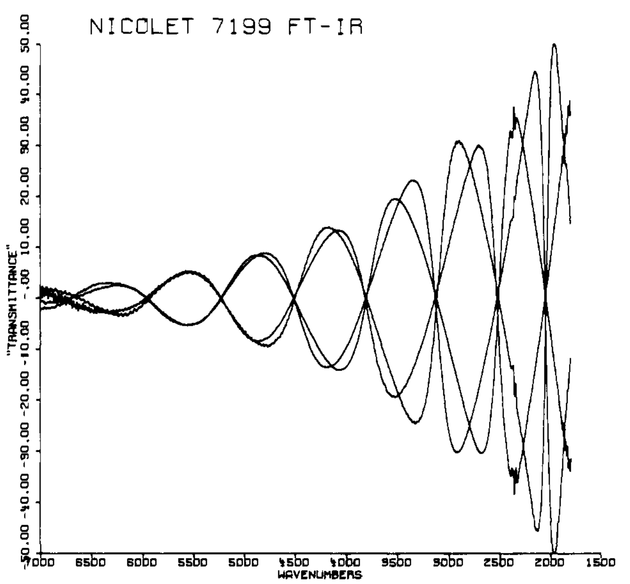

Figure 1. Four calibration curves where mirror image pairs are generated from the parallel and perpendicular position of the second polarizer with respect to the first. Pairs with shifted maxima are generated by exchanging the fast and slow axes of the retardation plate. Each curve represents 32 scans, with 0.145-cm/s mirror velocity, lock-in time constant of 0.7 ms, total measurement time of 90.3 s, small source aperture, and small area InSb detector.

The experimental method involves modulating the infrared beam between left and right circular polarization states at a frequency of 50 kHz, significantly higher than the Fourier interferogram frequencies. By first electronically demodulating the detector signal with a lock-in amplifier tuned to 50 kHz, a *new* interferogram is obtained representing the CD of the sample.[1] The components used in this experiment were a Nicolet 7199 FT IR spectrometer with a water-cooled glower source and a Ge-coated KBr beam splitter. Circular polarization was achieved with a BaF_2 wire grid polarizer (Molectron Corp.) and ZnSe photoelastic modulator.[4d,f] Intensities were measured with either a small area (1 mm^2, Nicolet) or a large area (144 mm^2, Spectronics, Inc.) InSb detector. Demodulation was achieved by a narrow band-pass 50-kHz filter and a lock-in amplifier (Princeton Applied Research Corp, Model 124A).

Figure 1 shows four CD calibration curves obtained by placing a sapphire retardation plate followed by a second BaF_2 polarizer in the sample position of the spectrometer. The theory of this measurement[1a,3b,6] and a dispersive spectrum[3b] have been published previously and the curve crossings above and below zero represent approximately unit CD magnitude. The calibration curves were optimized for magnitude by varying the interferometer mirror velocity, high and low pass electronic filters, retardation strength of the modulator, and time constant of the demodulating lock-in. The attenuation toward higher frequencies is due primarily to electronic filtering. The unusual nature of the CD interferogram, which results in positive and

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