

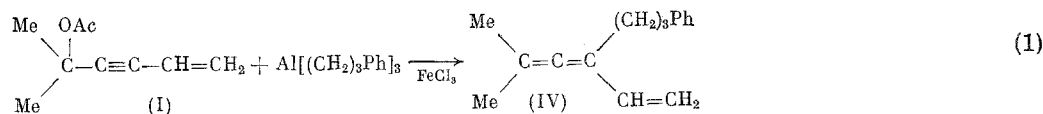
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## OXIDATION OF COUPLED VINYLALLENES AS A METHOD OF SYNTHESIS OF CYCLOPENTENONE DERIVATIVES

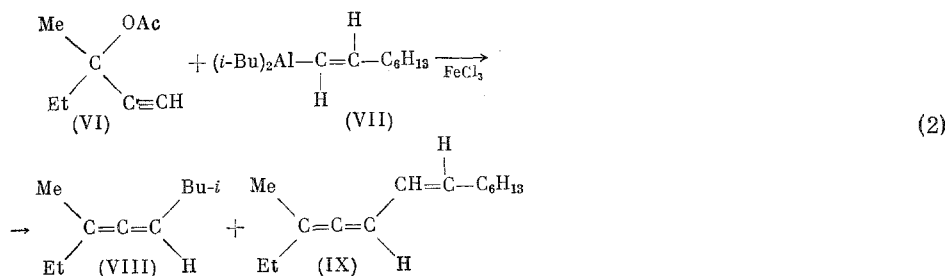
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547.514.714.6

Oxides of vinylallenes are reactive compounds which can rearrange to form cyclopentenone derivatives [1]. However this reaction is limited by the inaccessibility of substituted vinylallenes. The method developed by us of synthesis of substituted allenes from propynyl acetates and organoaluminum compounds (OAC) affords coupled vinylallenes of various structures [2]. By this method 2-methyl-4-ethyl-2,3,5-hexatriene (II), 2-methyl-4-hexyl-2,3,5-hexatriene (III), and vinylallene (IV) were obtained from 5-acetoxy-5-methyl-hex-3-ene (I).



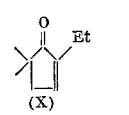
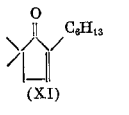
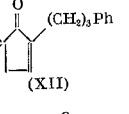
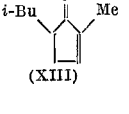
Reaction of 3-acetoxy-3-methyl-1-pent-4-ene with triisobutylaluminum leads to 3,7-dimethyl-1,3,4-octatriene (V) [3]. The high reactivity and accessibility of dialkylalkenylalanes make vinyl OAC's useful for organometallic synthesis [4], particularly for synthesis of vinylallenes. Thus, reaction of 3-acetoxy-3-methyl-1-pentyne (VI) with diisobutyl-E-octenyl-aluminum (VII), obtained by [5], gives allenes with isobutyl (VIII) and E-octenyl (IX) substituents in the ratio 13 : 87.



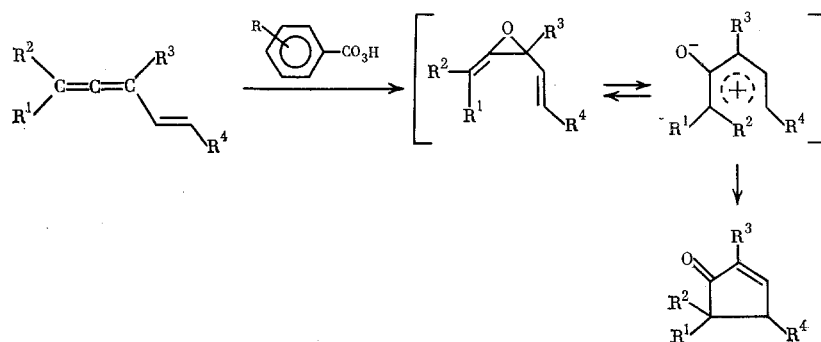
Thus, synthesis of vinylallenes can be carried out by introducing the alkyl substituent of the OAC into a vinyl-propynyl compound, or by introducing the vinyl radical of the Al-reagent into a propynyl system. We studied the oxidation of vinylallenes containing mono-(II)-(V) and disubstituted (IX) ethylene groups. In [6, 7] data on the oxidation of vinylallenes by p-nitro- and m-chloroperbenzoic acids are shown and in [8] data on the oxidation of vinylallene alcohols by tert-butyl hydroperoxide are presented. We studied the possibility of performing these reactions with perphthalic (PPA) and p-methoxycarbonylperbenzoic (MCPBA) acids [9].

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TABLE 1. Dependence of the Yield of 2,3-Cyclopentenone Derivatives on the Peracid Used during Oxidation of Vinylallenes

Vinylallene	Cyclopentenone	Yield after oxidation, %	
		PPA	MCPBA
$\begin{array}{c} \text{Et} \\   \\ \text{Me}_2\text{C}=\text{C}=\text{C} \\   \\ \text{CH}=\text{CH}_2 \\ \text{(II)} \end{array}$	 (X)	58	42
$\begin{array}{c} \text{C}_6\text{H}_{13} \\   \\ \text{Me}_2\text{C}=\text{C}=\text{C} \\   \\ \text{CH}=\text{CH}_2 \\ \text{(III)} \end{array}$	 (XI)	65	62
$\begin{array}{c} (\text{CH}_2)_3\text{Ph} \\   \\ \text{Me}_2\text{C}=\text{C}=\text{C} \\   \\ \text{CH}=\text{CH}_2 \\ \text{(IV)} \end{array}$	 (XII)	67	53
$\begin{array}{c} \text{Me} \quad \text{Bu-i} \\ \diagdown \quad / \\ \text{C}=\text{C}=\text{C} \\ / \quad \backslash \\ \text{H}_2\text{C}=\text{CH} \quad \text{H} \\ \text{(V)} \end{array}$	 (XIII)	56	41

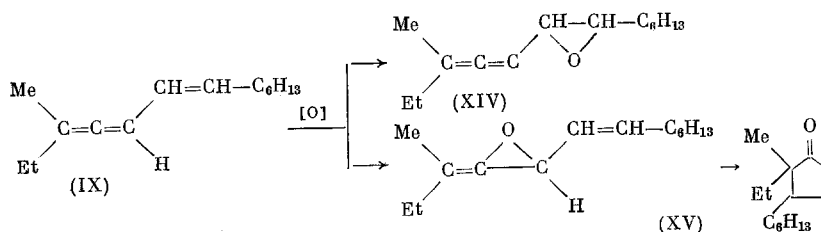
Oxidation of vinylallenes involves formation of the allene oxide followed by cyclization into the cyclopentenone.



(3)

$R^1, R^2, R^3, R^4 = \text{Alk}; R = \text{COOH}, \text{COOMe}.$

Oxidation of vinylallenes was carried out at 10°C in  $\text{CH}_2\text{Cl}_2$  with a 1.5-fold excess of MCPBA or at 20°C with a 1.5-2 fold excess of ethereal PPA. In the case of allenes with an unsubstituted vinyl group (II)-(V) the main oxidation products are 2,5-substituted cyclopentenones. However the reaction is complicated by formation of ketobenzoates or acid phthalates. Formation of a mixture of ketobenzoate isomers during peracid oxidation of vinylallenes was observed earlier in [6, 7]. Acid ketophthalates formed upon oxidation by PPA separate during the following alkaline treatment, which makes the purification of the cyclopentenones significantly easier. Upon oxidation by MCPBA isolation of the substituted cyclopentenones was effected by chromatography. The yields of the obtained compounds are shown in Table 1. Characteristic absorption bands in the IR spectra at 1710 and 1640  $\text{cm}^{-1}$  and the UV absorption maxima at 229-230 nm,  $\epsilon = (9-11) \cdot 10^3$  confirm the formation of coupled cyclopentenones. For allene (IX) having a substituted vinyl group (i.e. nucleophilic double bond), the probability of formation of epoxide (XIV) increases. This can become the predominant reaction [7]



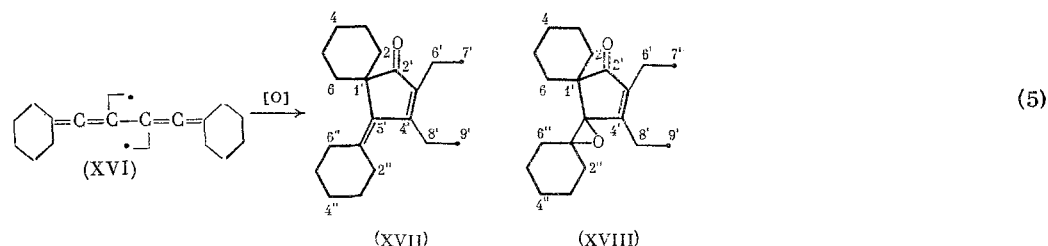
(4)

TABLE 2. Physical Constants and Spectral Characteristics of Substituted Cyclopentenones

Compound	Boiling point, C (p, mm Hg)	$n_D^{20}$	IR spectrum, $\nu$ , cm <sup>-1</sup>	NMR spectrum <sup>1</sup> H and <sup>13</sup> C, $\delta$ , ppm	UV spectrum, $\lambda_{max}$ , nm ( $\epsilon$ )	Mass spectrum, m/z
2-Ethyl-5,5-dimethylcyclopent-2-en-1-one (X)	45-46 (5)	1,4596	1710 1640 3040 840	<sup>1</sup> H: 1,02 s (6H, CH <sub>3</sub> ), 1,05 t (3H, CH <sub>2</sub> , J=7Hz), 2,03 m and 2,34 m (4H, CH <sub>2</sub> C=C), 7,05 m (1H, CH=C)	230 (9852)	138
2-Hexyl-5,5-dimethylcyclopent-2-en-1-one (XI)	62-63 (0,5)	1,4590	1715 1640 3050 840	<sup>1</sup> H: 0,87 t (3H, CH <sub>3</sub> , J=6 Hz), 1,02 s (6H, CH <sub>3</sub> ), 1,28 s (8H, CH <sub>2</sub> ), 2,03 m; 2,34 m (4H, CH <sub>2</sub> C=C), 7,06 m (1H, CH=C)	230 (11 720)	194
2-(3-Phenylpropyl)-5,5-dimethylcyclopent-2-en-1-one (XII)		1,5228	1710 1640 1605 3030 3070 3090 840 705	<sup>1</sup> H: 1,00 s (6H, CH <sub>3</sub> ), 1,14 s (2H, CH <sub>2</sub> ), 1,55 m (2H, CH <sub>2</sub> ), 2,26 m (2H, CH <sub>2</sub> C=C), 2,46 t (2H, CH <sub>2</sub> C=C, J=7 Hz), 6,90 (1H, CH=C), 7,05 s (5H, Ph)	211 (9590) 230 (7482)	228
2-Methyl-5-iso-butylcyclopent-2-en-1-one (XIII)	74-75 (10)	1,4640	1710 1640 3040 840	<sup>1</sup> H: 0,90 d (6H, CH <sub>3</sub> , J=6 Hz), 1,44-1,87 m (3H, CH; CH <sub>2</sub> ), 1,67 m (3H, CH <sub>3</sub> ), 2,20 m (2H, CH <sub>2</sub> C=C), 2,50 m (1H, CHCO), 7,12 m (1H, CH=C)	229 (8920)	152
Cyclohexaspiro-1'-(2'-oxo-3',4'-diethyl-3'-cyclopenten)-5'-spirooxiranspiro-cyclohexane (XVIII)	M. p. 47-49		1690 1640 3058 1450 1380 1186 1058	<sup>1</sup> H: 1,00 t (3H, CH <sub>3</sub> , J=7 Hz), 1,05 t (3H, CH <sub>3</sub> , J=7,5 Hz), 1,60 m (16H, CH <sub>2</sub> ; 4H, CH <sub>2</sub> CO), 2,24 q (2H, CH <sub>2</sub> , J=7 Hz), 2,34 q (2H, CH <sub>2</sub> , J=7 Hz), <sup>13</sup> C: 12,99 q (C <sup>7'</sup> ), 13,32 q (C <sup>8'</sup> ), 29,28 t (C <sup>3'</sup> ), 29,70 t (C <sup>6'</sup> ), 16,91 t, 21,28 t, 21,67 t, 21,74 t, 24,81 t, 25,16 t, 25,29 t, 25,78 t, 31,30 t, 33,91 t (C <sup>2'-C<sup>6'</sup></sup> ), (C <sup>2''-C<sup>6''</sup></sup> ), 47,88 s (C <sup>1'</sup> ), 69,65 s (C <sup>1''</sup> ), 77,71 s (C <sup>5'</sup> ), 145,63 s (C <sup>5''</sup> ), 166,36 s (C <sup>4'</sup> ), 209,73 s (C <sup>2'</sup> )	246 (10 198)	302

Upon oxidation of allene (IX) by MCPBA cyclopentenone (XV) is isolated in a yield of 15% and PPA (XV) generally is not formed. Probably the reaction proceeds with formation of unstable epoxide (XIV) which is opened by acids with formation of hydroxy benzoates or hydroxyphthalate. Also the oxidation of vinylallenes by tert-butyl hydroperoxide (TBHP) was carried out in the presence of Mo(CO)<sub>6</sub> and from allenes (II) and (III) the corresponding cyclopentenones were obtained with 25-30% yield. In this case the reaction is complicated by formation of a significant amount of polymeric products.

The oxidation of diallenes, the synthesis of which is presented in [3], by an equimolar amount of PPA in ether proceeds significantly faster than that of vinylallenes and is complete at 20°C after 2-5 h. Oxidation of 3,8-dimethyl-5,6-diethyl-3,4,6,7-decatetraene, as in the case of allene (IX) produced a mixture of products in which cyclopentenone was not found. Upon oxidation of 1,1,6,6-dipentamethylene-3,4-diethyl-1,2,4,5-hexatetraene (XVI) a mixture of ketone (XVII) and epoxyketone (XVIII) was formed. The reaction mixture was oxidized by an excess of PPA, which resulted in epoxyketone (XVIII) with 28% yield.



The characteristics of the substituted cyclopentenones are shown in Table 2.

## EXPERIMENTAL

UV and IR spectra were recorded on a Specord UV-VI S (solution in ethanol) and a UR-20 (in thin layer) spectrometers. PMR spectra were obtained with Tesla instruments (60 and 100 MHz) on solutions in  $\text{CCl}_4$  relative to TMS. Mass spectra were obtained on a MX-1306 spectrometer at 70 eV. Temperature of ionization chamber was 150°C.  $^{13}\text{C}$  NMR spectra were recorded on solutions in  $\text{CDCl}_3$  with a Jeol FX-90 Q radio-spectrometer (22.63 MHz). Gas-liquid chromatography was carried out on a Chrom-5 instrument on 1.3 m  $\times$  3 mm and 2.4  $\times$  3 mm columns containing 5% SE-30 on N-AW-CMCS Chromaton, with He carrier gas (50 ml/min).

Synthesis of vinylallenes was carried out by the method of [2]. Allenes (IV) and (IX) were isolated by chromatography on silica gel using pentane eluant. Physical constants and spectral characteristics for allenes (II) and (III) are presented in [2], and for (II) in [3].

**2-Methyl-4-vinyl-7-phenyl-2,3-heptadiene (IV):** yield 34%,  $n_D^{20}$  1.5375. IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 3090, 3070, 3030, 1940, 1610, 1585, 995, 900, 750, 705. PMR spectrum ( $\delta$ , ppm): 1.72 s (6H,  $\text{CH}_3$ ), 2.07 m (2H,  $\text{CH}_2$ ), 2.56 m (4H,  $\text{CH}_2\text{Ph}$  and  $\text{CH}_2\text{C}=\text{C}$ ), 4.92 m and 6.15 m (3H,  $\text{CH}=\text{CH}_2$ ), 7.15 m (5H, Ph).  $m/z$  212.

**3,7-Dimethyl-3,4-octadiene (VIII):** IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1960. PMR spectrum ( $\delta$ , ppm): 0.92 d (6H,  $\text{CH}_3$ ,  $J=7$  Hz), 0.99 t (3H,  $\text{CH}_3$ ,  $J=6$  Hz), 1.33 m (1H, CH), 1.63 d (3H,  $\text{CH}_3$ ,  $J=3$  Hz), 1.91 m (4H,  $\text{CH}_2-\text{C}=\text{C}$ ), 4.90 m (1H,  $\text{CH}=\text{C}=\text{C}$ ).  $m/z$  138.

**3-Methyl-3,4,6-tridecatriene (IX):** b.p. 74-75°C (0.5 mm),  $n_D^{20}$  1.4885. IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 1950, 3020, 1650, 970. PMR spectrum ( $\delta$ , ppm): 0.83 t (3H,  $\text{CH}_3$ ,  $J=7$  Hz), 1.25 m (8H,  $\text{CH}_2$ ), 1.62 d (3H,  $\text{CH}_3$ ,  $J=1.5$  Hz), 1.98 m (4H,  $\text{CH}_2\text{C}=\text{C}$ ), 5.50 m (1H,  $\text{CH}=\text{C}=\text{C}$ ), 5.63 m (2H,  $\text{CH}=\text{CH}$ ). UV spectrum:  $\lambda_{\text{max}}$  221 nm,  $\epsilon$  14650,  $m/z$  192.

**Oxidation of vinylallenes by perphthalic and p-methoxycarbonylperbenzoic acids.** To vinylallene (5 mmole) an ether solution of PPA (7.5-10 mmole) was added at 0°C and maintained at 20°C for 24 h, or to a solution of vinylallene (5 mmole) in 15 ml  $\text{CH}_2\text{Cl}_2$  MCPBA (7.5 mmole) was added at 0°C and maintained at 10°C for 48 h. The reaction mixture in both cases was filtered and the residue was washed with ether. The solutions were washed with 5% NaOH and water, dried with  $\text{MgSO}_4$ , evaporated, and distilled (PPA oxidation) or separated on a column with silica gel (MCPBA oxidation). For cyclopentones the eluant was pentane-ether (5:1) and for ketobenzoates it was pentane-ether (3:1). The mixtures of ketobenzoate isomers were not separated. In IR spectra of the mixtures intense absorption bands were observed at 1730, 740, and 3030-3100  $\text{cm}^{-1}$ , which corresponds with the complex ether group and the aromatic fragment. PMR spectra of the mixtures contain a singlet at 3.81 ppm ( $\text{COOCH}_3$ ) and a multiplet at 8.01 ppm (Ph). The IR spectrum of the allene (IX) oxidation products (by MCPBA) besides the above absorption frequencies also contain a band at 3500  $\text{cm}^{-1}$  (OH group), which indicates formation of oxybenzoates.

**4-Hexyl-5-methyl-5-ethylcyclopent-2-en-1-one (XV):** IR spectrum ( $\nu$ ,  $\text{cm}^{-1}$ ): 3050, 1715, 1635, 1600, 1470, 730. PMR spectrum ( $\delta$ , ppm): 0.82 t (6H,  $\text{CH}_3$ ,  $J=7$  Hz), 1.11 s (3H,  $\text{CH}_3$ ), 1.25 m (12H,  $\text{CH}_2$ ), 1.84 m (1H, CH), 5.83 m (1H,  $\text{CH}=\text{C}$ ), 7.33 m (1H,  $\text{C}=\text{CH}$ ).  $m/z$  208.

**Oxidation of diallene (XVI) by PPA.** The presence of a mixture of cyclohexanspiro-1'-(2'-oxo-3', 4'-diethyl-5'-cyclohexyliden-3'-cyclopentene (XVII) and (XVIII) in a 3:2 ratio was indicated by the  $^{13}\text{C}$  NMR spectrum and by UV and mass spectra.  $^{13}\text{C}$  NMR spectrum ( $\delta$ , ppm) for ketone (XVII): 13.46 q ( $\text{C}^7$ ), 13.74 q ( $\text{C}^9$ ), 29.11 t ( $\text{C}^8$ ), 29.73 t ( $\text{C}^6$ ), 16.29 t, 21.67 t (2C), 23.04 t, 26.61 t, 28.43 t, 29.73 t (2C), 32.90 ( $\text{C}^2-\text{C}^6$  and  $\text{C}^{2''}-\text{C}^{6''}$ ), 48.83 s ( $\text{C}^{1'}$ ), 137.64 s ( $\text{C}^{1''}$ ), 139.17 s ( $\text{C}^5$ ), 140.48 s ( $\text{C}^{3'}$ ), 165.71 s ( $\text{C}^{4'}$ ), 211.07 s ( $\text{C}^{2'}$ ). UV spectrum for (XVII):  $\lambda_{\text{max}}$  213, 305 nm.  $m/z$  286.

**Oxidation of vinylallenes by tert-butyl hydroperoxide.** To vinylallene (4 mmole) in 5 ml of dry benzene  $2.2 \cdot 10^{-2}$  mmole  $\text{Mo}(\text{CO})_6$  was added and 98% TBHP (6 mmole) in 2 ml benzene was added dropwise. The mixture was boiled for 5-6 h, cooled, washed with 5%  $\text{Na}_2\text{CO}_3$  and water, dried with  $\text{MgSO}_4$ , and evaporated. The obtained cyclopentenones were purified by chromatography on a column with  $\text{Al}_2\text{O}_3$  by elution with pentane-ether (5:1).

## CONCLUSIONS

Oxidation of coupled vinylallenes and diallenes by perphthalic and methoxycarbonylperbenzoic acids is a method of synthesis of substituted cyclopentanones.

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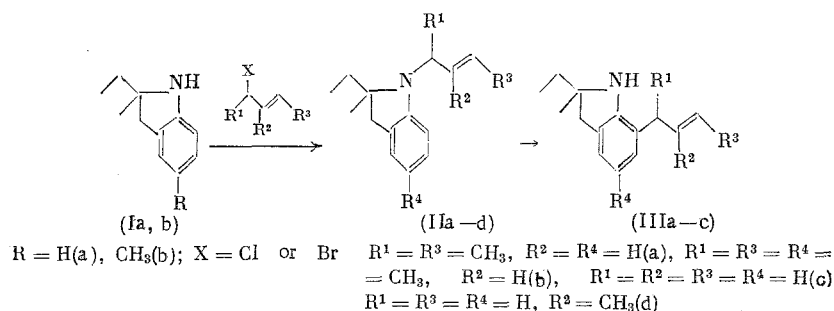
CLAISEN REARRANGEMENT OF STERICALLY HINDERED  
N-ALKENYLINDOLINES

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Despite the development of several methods for carrying out the amino-Claisen rearrangement [1, 2], this reaction remains insufficiently studied, especially for the series of nitrogen-containing heterocyclic compounds. In the present paper our goal was to investigate the Claisen rearrangement in a series of sterically hindered 2-methyl-2-ethyl- (Ia) and 2,5-dimethyl-2-ethylindolines (Ib) in order to elucidate its feasibility for the synthesis of complex heterocyclic derivatives.

In most cases, N-alkenylated materials are required for carrying out Claisen rearrangements. Indolines (Ia, b) are N-alkenylated under harsher conditions than necessary for aromatic amines [3].



Thus, (IIa-d) were prepared by heating indolines (Ia, b) with alkenyl halides, specifically, allyl bromide, methallyl chloride, and 4-chloro-2-pentene, at 150°C in an autoclave. Compounds (IIa and b) underwent rearrangement at room temperature in the presence of mineral acids to give 2-methyl-2-ethyl-7-(1'-methyl-2'-butenyl)- (IIIa) and 2,5-dimethyl-2-ethyl-7-(1'-methyl-2'-butenyl)indoline (IIIb) in 90% yields [4]; in contrast, N-allylanilines rearrange at significant rates only upon heating above 100°C [5, 6].

The ease of this isomerization process was further demonstrated by the rearrangement of the hydrochloride salt of (IIc) to give (IIIc) at 150°C; the hydrochloride salt of N-allylaniline does not rearrange under these conditions. Heating allyl bromide with excess indoline (Ia) also led to rearrangement to give (IIIc). Monitoring this reaction by GLC revealed the stable presence of (IIc) in the reaction mixture. Apparently, the limiting step of this process is the rearrangement step, since treatment of 4-chloro-2-pentene with (Ia, b) led to the

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