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π-ALLYLMETAL CHEMISTRY

V *. NEW π-ALLYLPALLADIUM(II) COMPLEXES AS MODELS OF KEY INTERMEDIATES IN ALLYLIC ALKYLATION

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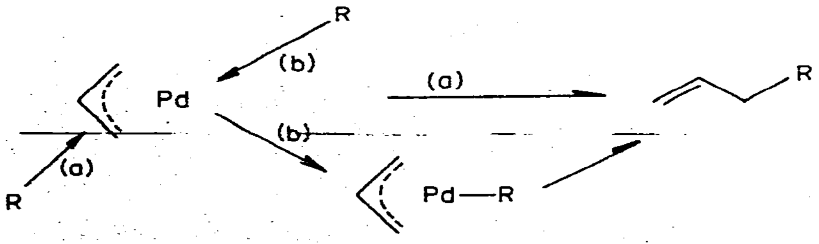
Summary

Novel complexes of the type Pd(π-all)(Ar)(L) (all = $CH_2{=}CMeCH_2$, $MeCH{=}CHCH_2$, $EtO_2CCH{=}CHCH_2$; Ar = C_6Cl_5, 2,3,5,6-C_6HCl_4; L = PPh_3, $SbPh_3$) were prepared and characterized by ^1H NMR spectroscopy. These were shown to be particularly good model compounds for mechanistic studies of allylic alkylation via π-allylpalladium complexes. Reductive elimination of these complexes proceeds by a unimolecular, concerted pathway to give, in a regio- and stereo-selective fashion, quantitative yields of allylpolychlorobenzenes.

Introduction

Numerous reactions are known [1] forming carbon—carbon bonds via nucleophilic attack of carbanions on π-allylpalladium(II) complexes. In these reactions, the site (carbon or palladium) of initial attack of the nucleophile is believed to be determined by the nature of the nucleophile and/or the coordination environment.

Trost et al. have shown [1a] that the alkylation using a soft carbanion proceeds by path (a) with attack of the nucleophile from the backside of the π-allyl plane with respect to Pd, especially in the presence of an excess of the ligand.



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* For part IV see ref. 9.

However, the potential importance of path (b) under different conditions * has not yet been appreciated, partly because the instability of possible intermediates involved in this path precludes mechanistic studies. In order to obtain a more explicit view of the mechanism of path (b), we have chosen polychlorophenyl groups (Ar) as nucleophiles. The work reported here deals with the preparation of a series of fairly stable Pd(π-all)(Ar)(L) complexes (all = $CH_2{=}CMeCH_2$, $MeCH{=}CHCH_2$, $EtO_2CCH{=}CHCH_2$; Ar = C_6Cl_5, 2,3,5,6-C_6HCl_4; L = PPh_3, $SbPh_3$) and the coupling of π-allyl and Ar groups induced by thermal decomposition of these complexes.

Experimental

^1H NMR spectra were recorded on a Japan Electron Optics JNM-PS-100 spectrometer with tetramethylsilane as internal standard. Infrared spectra were run on a Hitachi 225 spectrophotometer as nujol mulls. Molecular weights were determined using a Mechrolab vapor pressure osmometer Model 302. The mass spectra were measured on a Hitachi Mass spectrometer Model RMU-6E. Analytical data and molecular weights are summarized in Table 1. Literature methods were used to prepare the starting complexes Pd(π-all)(Cl)(L) [3]. Tetrahydrofuran was distilled from $LiAlH_4$ prior to use.

Pd(π-all)(2,3,5,6-C_6HCl_4)(L)

A series of (π-allyl)(2,3,5,6-tetrachlorophenyl)palladium(II) complexes I—V were prepared from Pd(π-all)(Cl)(L) and Tl(2,3,5,6-C_6HCl_4)$_3$ in a manner similar to that for Pd(π-C_3H_5)(C_6HCl_4)(PPh_3) [4].

TABLE 1

PROPERTIES AND ANALYTICAL DATA OF Pd(π-all)(Ar)(L)

Compound				M.p. [a] (°C)	Analysis (found (calcd.)) (%)		Mol. wt. [b]	
All	Ar	L			C	H	found (calcd.)	conc. mol %
2-MeC_3H_4	C_6HCl_4	PPh_3	I	150	52.45 (52.66)	3.48 (3.63)	654 [c] (639)	0.166
2-MeC_3H_4	C_6HCl_4	$SbPh_3$	II	140	46.37 (46.10)	2.98 (3.18)	734 (729)	0.126
1-MeC_3H_4	C_6HCl_4	PPh_3	III	114	52.64 (52.66)	3.54 (3.63)	616 (639)	0.108
1-MeC_3H_4	C_6HCl_4	$SbPh_3$	IV	110	45.86 (46.10)	3.04 (3.18)	741 (729)	0.131
1-$EtO_2CC_3H_4$	C_6HCl_4	PPh_3	V	149	51.65 (51.72)	3.37 (3.62)		
2-MeC_3H_4	C_6Cl_5	PPh_3	VI	148	50.10 (49.97)	3.29 (3.29)	675 (673)	0.105

[a]. With decomposition. [b] Determined in benzene at 25°C unless stated otherwise. [c] In chloroform at 38°C.

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* Reductive coupling of allylpalladium acetylacetonate induced by CO was suggested to proceed through path (b) [2]. The reaction of crotylpalladium chloride with Ph_2Hg to yield crotylbenzene [1e] also could occur via this pathway.

$Pd(\pi\text{-}2\text{-}MeC_3H_4)(C_6Cl_5)(PPh_3)$ (VI)

To a THF solution (70 ml) of pentachlorophenyllithium which was obtained from hexachlorobenzene (900 mg, 4.1 mmol) and an equimolar amount of commercial n-butyllithium in n-hexane, was added dropwise $Pd(\pi\text{-}2\text{-}MeC_3H_4)(Cl)(PPh_3)$ (1100 mg, 2.4 mmol) in THF (100 ml) under nitrogen at —78°C. Rapid stirring at this temperature was continued for 1 h. The reaction mixture was allowed to warm to room temperature and the solvent was removed in vacuo. The yellow residue thus obtained was extracted with benzene (20 ml) and was purified by chromatography through a short alumina column. Solid products obtained by evaporating the solvent were recrystallized from benzene/methanol to give yellow crystals of VI (850 mg, 53%).

Thermal decomposition of Pd(π-all)(Ar)(L)

In a typical reaction, an *o*-dichlorobenzene solution containing $Pd(\pi\text{-}2\text{-}MeC_3H_4)(C_6Cl_5)(PPh_3)$ (0.2 *M*) was heated at 150° C in a degassed sealed tube for 5 minutes to give a dark brown solution accompanied by the deposition of a palladium mirror. When pyrolysis was carried out in the presence of added PPh_3 (more than 1 mol per Pd atom), metallic palladium did not deposit. The tube was cooled and opened. The yield of 2-methylallylpentachlorobenzene was determined to be 99% by ^1H NMR spectroscopy using methyl β-naphthyl ether as internal standard. Evaporation of the solvent in vacuo and sublimation of the residue at 0.001 Torr and 95° C gave white solids which were recrystallized from chloroform/n-hexane to give colorless crystals, m.p. 80° C. (Found: C, 39.33; H, 2.24. $C_{10}H_7Cl_5$ calcd.: C, 39.45; H, 2.32%.) ^1H NMR ($CDCl_3$) δ (ppm) 1.84(s)(CH_3—), 3.68(s)(—CH_2—), 4.28(s) and 4.80(s)(CH_2=). Mass spectrum: M^+ 302, $(M - Cl)^+$ 267, $(M - 2\,Cl)^+$ 232 (*m/e* values are based on ^{35}Cl).

trans-$MeCH{=}CHCH_2C_6HCl_4$ was obtained similarly from a mixture of IIIa and IIIb, m.p. 45° C. (Found: C, 44.67; H, 2.87. $C_{10}H_8Cl_4$ calcd.: C, 44.49; H, 2.99%.) ^1H NMR ($CDCl_3$) δ (ppm) 1.64(d), J_H 6 Hz, (CH_3—), 3.68(d) J_H 5 Hz (—CH_2—), 5.20—5.50(m)(—CH=CH—), 7.36(s)(C_6HCl_4). The IR spectrum exhibited one strong band at 960 cm^{-1}. Mass spectrum: M^+ 268, $(M - Cl)^+$ 233, $(M - 2\,Cl)^+$ 198.

$CH_2{=}CMeCH_2C_6HCl_4$ and $EtO_2CCH{=}CHCH_2C_6HCl_4$ were obtained quantitatively by the thermolysis of I and V, as confirmed by their ^1H NMR spectra. However, attempts to isolate analytically pure coupling products were unsuccessful due to difficulties in crystallization.

$CH_2{=}CMeCH_2C_6HCl_4$; ^1H NMR ($CDCl_3$) δ (ppm) 1.75(s)(CH_3—), 3.50(s)(—CH_2—), 4.23(s) and 4.73(s) (CH_2=), 7.40(s)(C_6HCl_4). Mass spectrum: M^+ 268, $(M - Cl)^+$ 233, $(M - 2\,Cl)^+$ 198.

trans-$EtO_2CCH{=}CHCH_2C_6HCl_4$; ^1H NMR ($CDCl_3$) δ (ppm) 1.20(t)($\underline{CH_3}$—CH_2), 3.87(d), J_H 6 Hz (—$CH_2C_6HCl_4$), 4.10(q)(—CH_2O), 5.68(d) J_H 16 Hz (OCC$\underline{CH}$=CH), 6.90(dt)(CH=$\underline{CH}$—CH_2), 7.48(s)(C_6HCl_4).

Thermal decomposition of a mixture of $Pd(\pi\text{-}C_3H_5)(C_6HCl_4)(PPh_3)$ and VI

A 4/1 mixture of $Pd(\pi\text{-}C_3H_5)(C_6HCl_4)(PPh_3)$ (250 mg, 0.4 mmol) and VI (67 mg, 0.1 mmol) was heated at reflux in toluene (6 ml) for 0.5 h. The ^1H NMR spectrum of the reaction mixture showed that reductive elimination was complete with respect to the allyl and nearly half complete with respect to the 2-methylallyl complexes. Evaporation of the solvent and sublimation at 0.001 Torr and 95°C gave white solids, the mass spectrum of which showed peaks at *m/e* 302—312 due to $(MeC_3H_4C_6Cl_5)^+$ and at *m/e* 254—262 due to $(C_3H_5C_6HCl_4)^+$. Peaks at *m/e* 286—296 ascribable to $(C_3H_5C_6Cl_5)^+$ were absent. Confirmation of the absence of $(MeC_3H_4C_6HCl_4)^+$ (*m/e* 268—286) was hampered by the appearance of peaks at *m/e* 267—285 due to $(MeC_3H_4C_6Cl_5 - Cl)^+$.

Kinetic measurements

Known amounts of the palladium complex II and $SbPh_3$ were weighed into 1 ml of *o*-dichlorobenzene. The solution prepared in this way was sealed in an NMR tube in vacuo after degassing several times by the freeze-thaw-freeze method. The tube was immersed in a thermostatted oil bath, removed at appropriate intervals, and the ^1H NMR spectra were recorded. The rate was followed by monitoring the disappearance of the CH_3 singlet of II (δ 1.90 ppm) as well as by the appearance of the CH_3 singlet of the coupling product (δ 1.75 ppm) using methyl β-naphthyl ether as internal standard. The kinetics showed a first-order dependence on II in the range between 0.15 and 0.03 *M* initial concentration up to 70% decomposition. Typical kinetic plots are shown in Fig. 1. First-order rate constants obtained at various temperatures are 1.28×10^{-5} sec^{-1} (81°C), 4.37×10^{-5} sec^{-1} (92°C), 7.66×10^{-5} sec^{-1} (97°C), 12.78×10^{-5} sec^{-1} (102°C). Analysis of the kinetic data gave the activation parameters, $\Delta H^{\ddagger}$ (365 K) 28.2 kcal/mol and $\Delta S^{\ddagger}$ (365 K) —1.6 eu.

Reaction with maleic anhydride

I (64 mg, 0.1 mmol) and maleic anhydride (10 mg, 0.1 mmol) were dissolved in $CDCl_3$ (2 ml). As the reaction proceeded at room temperature, the solution grew pale green with deposition of palladium metal. After 12 h, the ^1H NMR spectrum of the reaction mixture showed that the reductive coupling was complete with quantitative formation of $2\text{-}MeC_3H_4C_6HCl_4$, using methyl β-naphthyl ether as internal standard. Similarly, III (32 mg, 0.05 mmol) and maleic anhydride

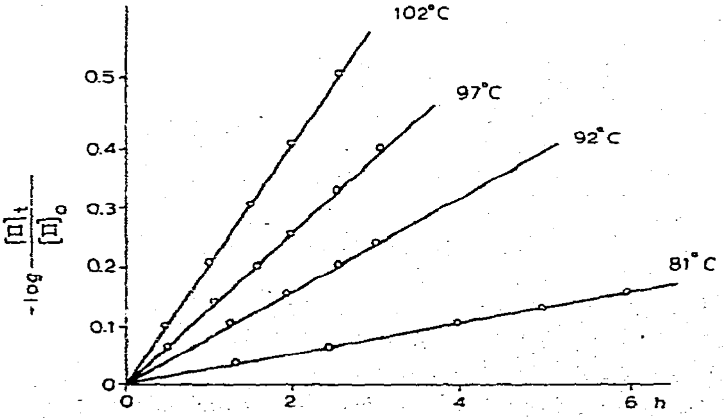
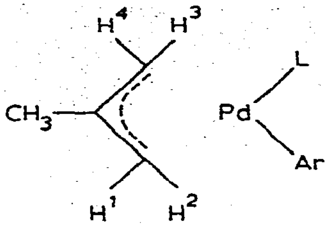
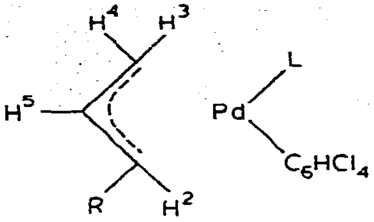


Fig. 1. First-order plots for the decomposition of $Pd(\pi\text{-}2\text{-}MeC_3H_4)(C_6HCl_4)(SbPh_3)$ in *o*-dichlorobenzene.

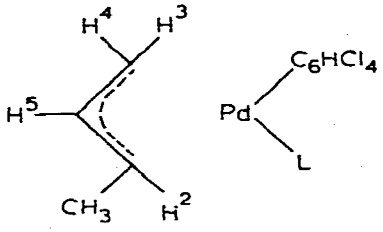
(5 mg, 0.05 mmol) were dissolved in 1 ml of $CDCl_3$. After 3 h, the ^1H NMR spectrum of the reaction mixture containing methyl β-naphthyl ether as internal standard showed the exclusive formation of $MeCH{=}CHCH_2C_6HCl_4$.



(I,II) Ar = C_6HCl_4
(VI) Ar = C_6Cl_5



(IIIa, IVa) R = CH_3
(V) R = CO_2Et

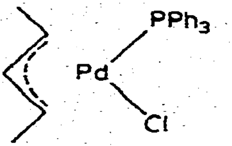


(IIIb, IVb)

Results and discussion

^1H NMR spectra of Pd(π-all)(Ar)(L) complexes

The ^1H NMR spectra of I—VI (Table 2) are reasonably interpreted in terms of a rigid π-allyl structure on the NMR time scale, as was the case for $Pd(\pi\text{-}C_3H_5)(C_6HCl_4)(PPh_3)$ [4]. The spectra show no temperature dependence in the range 23—80° C, even in the presence of a more than fivefold excess of ligands per atom palladium. The ^1H NMR spectra of the crotyl complexes III and IV indicate the existence of two kinds of geometrical isomers with the ratio being approximately 1/4.3 and 1/4 for L = PPh_3 and $SbPh_3$. On the grounds of preferential coupling of ^{31}P with allylic protons *trans* to the phosphine [3a], we determined that the methyl group of the major component is located *trans* to phosphine (IIIa) and that the methyl group of the minor component is *cis* to the phosphorus atom (IIIb). The magnitudes of $J(P—CH_3)$ in both IIIa and IIIb are nearly equal to those [3a] observed in the 1,3-dimethylallyl complex, VII. Therefore, it would be reasonable to assume that the methyl group is situated in the *syn* position in both IIIa and IIIb. The spectra of IVa and IVb were assigned on the basis of the similarity of the chemical shifts between the resonances in IVa, IVb and IIIa, IIIb.



(VII)

TABLE 2

100 MHz ^{1}H NMR DATA ^{a} FOR Pd(π-all)(Ar)(L) IN $CDCl_3$

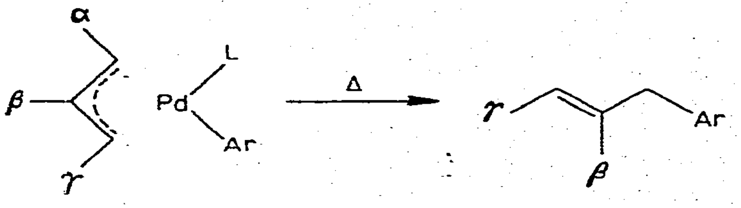
Compound	H(1)	H(2)	H(3)	H(4)	H(5)	CH_3	C_6HCl_4
I	3.96dd J_4 3 J_P 6	3.06d J_P 10	2.70s	3.61d J_1 3		1.92s	6.92s
II	4.10d J_4 3	3.17s	2.58s	3.96d J_1 3		1.92s	6.97s
IIIa		4.00m	2.38d J_5 13	3.46d J_5 7	5.21m	1.57dd J_2 6 J_P 9	6.93s
IIIb		b	2.82dd J_5 12 J_P 11	3.65dd J_5 8 J_P 12	b	1.13t J_2 6 J_P 9	b
IVa		4.14dq J_5 12 $J(CH_3)$ 6	2.42d J_5 13	3.90d J_5 7	5.18ddd J_2 12 J_3 13 J_4 7	1.64d J_2 6	7.00s
IVb		c	3.02d J_5 12	4.02d J_5 7	c	c	c
V		4.02dd J_5 12 J_P 9	3.00d J_5 14	3.82d J_5 8	6.28ddd J_2 12 J_3 14 J_4 8	0.84t ($\underline{CH_3}CH_2$-) 3.90q ($CH_3\underline{CH_2}O$-)	6.94s
VI	3.86dd J_4 3 J_P 6	2.98d J_P 9	2.66s	3.57d J_1 3		1.96s	

[a] Chemical shift in ppm downfield from TMS, J in Hz; s, singlet; d, doublet; t, triplet; m, multiplet; dd, doublet of doublets, dq, doublet of quartets; ddd, doublet of doublet of doublets; J_X = coupling constant with proton numbered X, J_P = coupling constant with ^{31}P. [b] Obscured by the resonances of IIIa. [c] Obscured by the resonances of IVa.

V exists as a single stereoisomer, a *syn*-COOEt configuration as shown by the magnitude of the coupling (12 Hz) between H(2) and H(5).

Reductive elimination induced by thermolysis

Thermolysis of the π-allyl complexes I—VI in *o*-dichlorobenzene resulted in complete reductive elimination of organic groups to give quantitative yields of allylpolychlorobenzenes which were characterized by ^{1}H NMR, mass spectra and/or satisfactory elemental analyses. In the pyrolysis of III, IV and V, carbon—carbon bond formation occurred exclusively at the less crowded terminal positions.



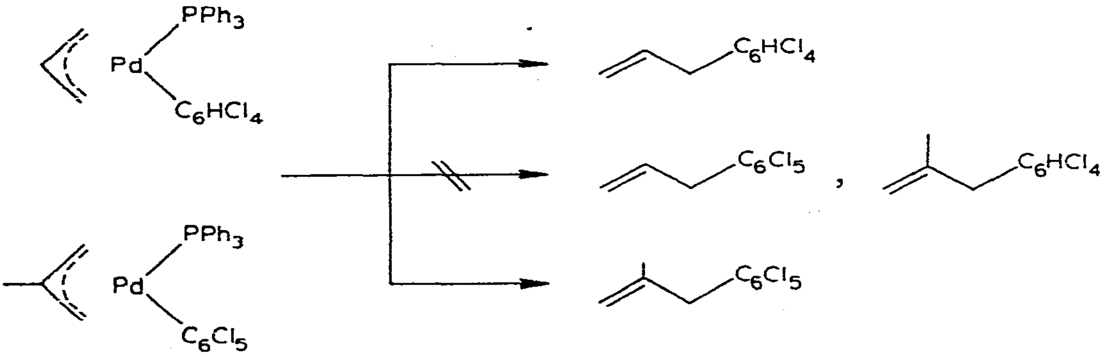
(1)

α = H or Me;
β = H or Me;
γ = H, Me or CO_2Et

The stereochemistry of $EtO_2CCH{=}CHCH_2C_6HCl_4$ and $MeCH{=}CHCH_2C_6HCl_4$ was assigned *trans* on the basis of the ^1H NMR spectrum (J(H—H) 16 Hz) of the former and the IR data (960 cm^{-1}) of the latter. Thus, the reaction proceeds completely regio- and stereo-selectively. Attempts were made to isolate the pyridine complex $Pd(\pi\text{-}2\text{-}MeC_3H_4)(C_6HCl_4)(py)$ from $Pd(\pi\text{-}2\text{-}MeC_3H_4)(Cl)(py)$ and $Tl(C_6HCl_4)_3$ in chloroform, but it is thermally far less stable, giving the coupling product in good yield even at 0° C.

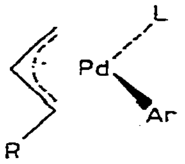
The observation that neither diallyl nor biaryl was formed in eq. 1 could exclude the possibility of homolytic fission of carbon—palladium bonds (free radical mechanism). The intramolecular nature of the reaction was demonstrated, as shown schematically (Scheme 1), by the absence of cross coupling products from a mixture of $Pd(\pi\text{-}C_3H_5)(C_6HCl_4)(PPh_3)$ and VI.

SCHEME 1

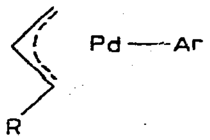


It was noticeable that the rate and the order (unimolecular) of the decomposition of II did not show any dependence on the amounts of $SbPh_3$ added (1—20 mole per atom Pd). Addition of PPh_3 to I up to tenfold excess also apparently had no significant effect on the rate of decomposition, although the reaction did not strictly follow the first order kinetics in this case. Such an absence of ligand dependence of the rate may be compared with two different, opposing patterns in the thermal decomposition of square planar organometallic compounds; the addition of excess phosphines was reported (i) to retard the elimination of alkanes from trialkylgold(III) [5] and (ii) to accelerate a similar process involving *cis*-$PtAr_2L_2$ complexes [6].

The reactivity patterns exhibited by the present allyl complexes, such that pyridine is more effective than are phosphines and that no excess of ligand is necessary for the coupling, apparently are different from those observed in the allylic alkylation by means of soft carbanions [1a], and thus may well be taken as indirect evidence to support the attack of the soft carbanion on carbon rather than palladium in the latter reactions. At present it is rather difficult to define a precise mechanism which can explain the regioselectivity observed in the decomposition of IIIa and V where the coupling occurred between the groups originally located *trans* to each other. The selective coupling could have readily occurred from IIIb and a geometrical isomer of V, if any, analogous to IIIb, but we have no ^1H NMR evidence for both the presence of this isomeric form of V and the occurrence of interconversion from IIIa to IIIb. One possible path without such prior *cis—trans* isomerization would involve distortion from the planar configuration (A). Alternative to this route is the decomposition via a three-coordinate intermediate (B), which involves ligand dissociation as the rate-determining step. We cannot discount this possibility, particularly since it has recently been reported [7] that the unimolecular ligand dissociation step is dominant in reactions of square planar complexes containing aryl groups.



(A)



(B)

Reductive elimination induced by maleic anhydride

The reductive elimination of (π-all)(Ar)Pd^{II} complexes I and III also could be induced by the addition of maleic anhydride to give quantitative yields of the coupling products at room temperature. In contrast, I was stable in chloroform at least for a week in the absence of maleic anhydride. It has been shown that the activation of the carbon—metal bond by coordination of electron-withdrawing olefins constitutes a crucial step in the reductive elimination of alkanes from NiR_2(dipy) induced by acrylonitrile, maleic anhydride and so on [8], but there was no ^1H NMR evidence in the present system to show any interaction between the olefin and the palladium atom. We are now investigating a precise mechanism regarding this maleic anhydride-induced allyl coupling reaction.

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