Direct Evidence of Cis Addition in the Catalytic Hydrocarboxylation of Acenaphthylene to Acenaphthene-1-carboxylic Acid

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The hydrocarboxylation of acenaphthylene with the $[PdCl_2(CH_3CN)_2] + nPAr_3$ catalytic system gave good yields of acenaphthene-1-carboxylic acid, after it was found that the chemoselectivity over oligomeric side products is highly dependent on the electronic characteristics of the phosphine and the P/Pd ratio. Deuteriocarboxylation of this substrate has been found useful to determine the diastereoselectivity of this type of reaction, owing to the structure of the product. A series of results showed that hydrocarboxylation of acenaphthylene with oxalic acid and CO at 30 bar is highly diastereoselective in the cis isomer under all tested conditions but one.

Introduction

Acenaphthylene is presented as an especially suited olefin for the study of the hydro-carboxy addition reaction[1] because of its symmetry and rigidity, and also because of the spectroscopic characteristics of the carboxylic acid product,[2] which allows the precise determination of the cis/trans nature of the addition in a straightforward manner. In 1975 Consiglio and Pino reported on the hydroesterification of 3-methyl-2-pentene catalyzed by $[PdCl_2(PPh_3)_2]$ under high CO pressure (over 300 bar).[3] The products were the methyl esters of the carboxylic acids 2-ethyl-2-methylbutanoic, 3-ethylpentanoic, 4-methylhexanoic, and 2,3-dimethylpentanoic as the major product. The fact that *trans*-3-methyl-2-pentene gave mainly the *threo*-2,3-dimethylpentanoate and *cis*-3-methyl-2-pentene gave mainly the *erythro* isomer stands as the reference that allows hydroesterification to be considered a stereoselective cis addition.[1l] However, a large number of variations have been developed in carbonylations of this type, and some may affect the very nature of the catalytic system, such as the addition of a second metal (Sn, Cu, Ni, ...) or the use of alternate carbonyl sources (formic or oxalic acids). In this line, we report on a simple method to obtain information on the inherent stereoselectivity of the catalytic reaction based on the use of acenaphthylene as a test olefin, a method that in principle could be of application to a variety of catalytic systems and reaction conditions.

Acenaphthene-1-carboxylic acid ($AnCO_2H$) is a synthetic challenge in itself. It is a simple molecule with potential applications related to its biological activity as a plant growth factor or as the acid part of amides with powerful analgesic properties.[4] However, $AnCO_2H$ is only available through a series of synthetic steps with rather low atom economy.[5] Hydroformylation with rhodium has been used to obtain acenaphthene-1-carboxaldehyde (AnCHO), but the oxidation to the

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Table 1. Palladium-Catalyzed Hydrocarboxylation of Acenaphthylene to $AnCO_2H$ with Arylphosphine Ligands of Different Electronic Properties[a]

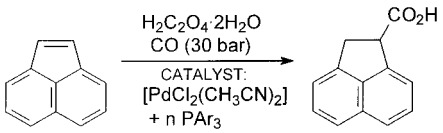
PAr_3	A (%)	P (%)	PAr_3	A (%)	P (%)
$P(C_6H_4\text{-}4\text{-}CH_3)_3$	21	79	$P(C_6H_4\text{-}4\text{-}CF_3)_3$	20	63
$P(C_6H_5)_3$	45	42	$P(C_6F_5)_3$	12	43
$P(C_6H_4\text{-}4\text{-}F)$	55	26			

[a] Definitions and conditions: A, $AnCO_2H$; P, polymer; catalyst $[PdCl_2(CH_3CN)_2]$ + 4 PAr_3; temperature 100 °C. See the Experimental Section.

target acid required three extra steps.[6] Catalytic hydrocarboxylation seems to be the reaction of choice to convert one of the simplest and cheapest sources of the acenaphthenic ring system, i.e., technical acenaphthylene from coal, to $AnCO_2H$. However, to the best of our knowledge, this synthetic approach has never been used, which is odd, since a number of olefins,[1] alcohols,[7] halides,[8] and even epoxides[9] have been carboxylated.

Results and Discussion

Assuming a low reactivity for this internal, albeit electron-rich olefin and a dependency of the activity of the palladium catalyst on the electronic nature of the modifying ligand, the study of this catalytic reaction was undertaken using a series of simple phosphines that span different electronic properties: $P(C_6H_4\text{-}4\text{-}Me)_3$, PPh_3 (L^H), $P(C_6H_4\text{-}4\text{-}F)_3$ (L^F), $P(C_6H_4\text{-}4\text{-}CF_3)_3$ and $P(C_6F_5)_3$:[1r]



It was found that conversion to $AnCO_2H$ is strongly dependent on this parameter, and the best results were obtained with L^H and L^F (Table 1). Acenaphthylene undergoes hydrocarboxylation to $AnCO_2H$, but polymerization was also observed; this is somewhat unusual for these reaction conditions and also for the comparatively large ligand-to-metal ratios used, which tend to disfavor chain growth. No other side products were observed in any significant amount. With L^H poly(acenaphthylene) was formed, but with L^F carbonylation oligomers and polymers were obtained; the factors that determine the formation and nature of these byproducts are still under study. Results in Table 2 show that even with L^H and L^F conversions to $AnCO_2H$ are quite variable, and there is a strong dependency of the chemoselectivity on the temperature and the P/Pd ratio. Presumably, the active species has two phosphines per palladium and a higher ligand/metal ratio is necessary to maximize its concentration when using the less basic fluorophosphine. In this line, L^F favors conversion to the acid at the lower temperature but requires a higher P/Pd ratio. The best result with L^F is found at 80 °C with L^F/Pd = 4, a 74% conversion to acid. The better ligand L^H used in excess seems to block the necessary coordination sites; therefore, it works better at lower P/Pd ratios. Also, with L^H conversions are larger at the higher temperature, probably because ligand dissociation is faster. The best result with L^H is obtained at 100 °C with L^H/Pd = 2, a 62% conversion to acid (Table 2).

Table 2. Palladium-Catalyzed Hydrocarboxylation of Acenaphthylene to $AnCO_2H$ with PPh_3 (L^H) and $P(C_6H_4\text{-}4\text{-}F)_3$ (L^F) Ligands[a]

	80 °C				100 °C			
	L^H		L^F		L^H		L^F	
[L]/[Pd]	A (%)	P (%)	A (%)	P (%)	A (%)	P (%)	A (%)	P (%)
2	43	24	53	27	**62**	16	38	31
3	16	36	63	10	56	38	34	49
4	6	36	**74**	15	45	42	55	26

[a] Definitions and conditions: A, $AnCO_2H$; P, polymer; catalyst $[PdCl_2(CH_3CN)_2]$ + n L (n = 2−4; L^H = $P(C_6H_5)_3$; L^F = $P(C_6H_4\text{-}4\text{-}F)_3$. See the Experimental Section.

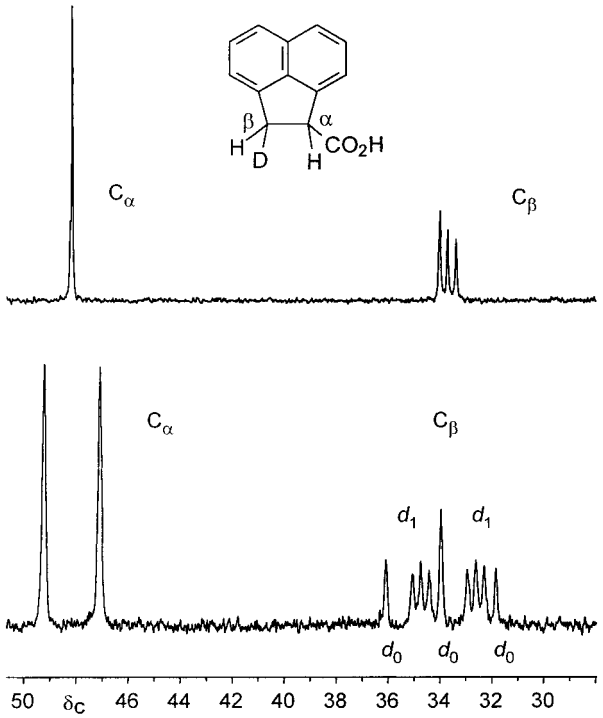


Figure 1. $^{13}C\{^1H\}$ and ^{13}C NMR (62.5 MHz, $CDCl_3$) of two representative samples of $AnCO_2H$-*d* obtained by deuteriocarboxylation. The ^1H-coupled spectrum of the sample (bottom) allows the resolved observation of the *d* and d_0 isotopomers. In the top spectrum, a smaller amount of the d_0 isotopomer in the sample adds to the intensity of the high-frequency branch of the triplet. Within the limits of detection, no signal for the $AnCO_2H$-d_2 isotopomer has been observed.

Deuteriocarboxylation of acenaphthylene resulted in the monodeuterated acid at the β-carbon in all cases. The ^{13}C NMR analysis of all isolated $AnCO_2H$-*d* products exhibited the 1:1:1 triplets of the monodeuterated isotopomer and the resonances of the residual $AnCO_2H$-d_0, but the $AnCO_2H$-d_2 isotopomer was absent within the limits of the attainable signal-to-noise ratio (Figure 1). Deuterium NMR revealed that the addition proceeds cleanly in a cis mode; the chemical shift difference

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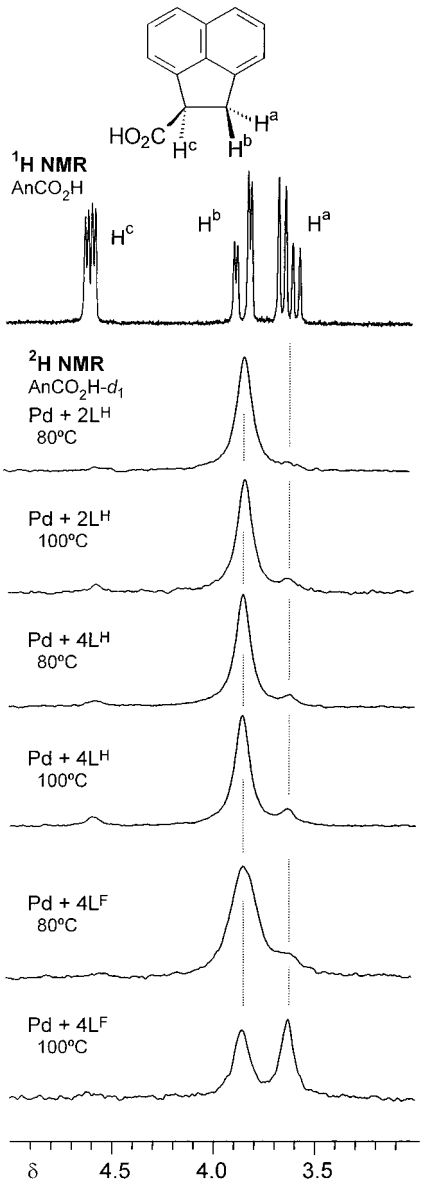
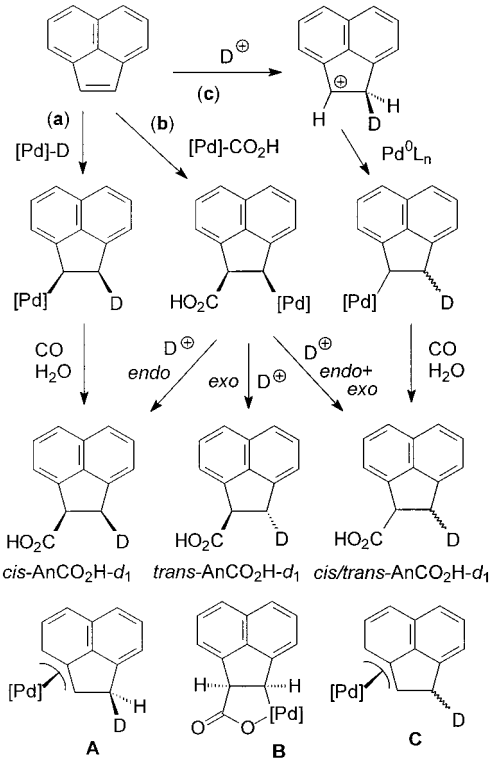


Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of $AnCO_2H$ and ^{2}H NMR (61 MHz, $CDCl_3$) spectra of $AnCO_2H$-*d* obtained under different conditions, as labeled. Deuterium is selectively incorporated in the *b* position, but only with L^F at 100 °C is it incorporated in either the *a* or the *b* position; very little or no deuterium is detectable in the *c* position under any conditions.

between H^a and H^b is large enough to avoid the superposition of the broad deuterium signals (Figure 2). Curiously, there is one exception: the reaction is not diastereoselective in the case of L^F at 100 °C.

There are two important mechanisms to explain catalytic hydrocarboxylation: the metal hydride mechanism and the (hydroxycarbonyl)metal complex mechanism, in addition to the now rarely invoked carbocation mechanism. These are sketched in Scheme 1, where the formation of the key palladium(II) alkyl intermediate has been emphasized. Current ideas are that either path a or path b could be acting, depending on the conditions (which are very variable in the literature) and the substrate.[1,10] A hydrido complex can first rise from the decomposition of a $PdL_n(COOH)^+$ complex into PdL_nH^+ and CO_2 or from the protonation of Pd^0L_n, formed in the reducing medium. The insertion of the olefin into

Scheme 1. Alkylpalladium Formation Routes to the Carboxylic Acid Product $AnCO_2H$[a]



[a] Legend: (a) hydride route; (b) hydroxycarbonyl route; (c) the carbocation route. [Pd] indicates palladium(II) and its phosphine ligands. Alternatively, the alkyl intermediates can be viewed as the allyl complexes $[Pd^{II}(\eta^3\text{-an})L_2]^+$ (**A** and **C**) or as the metallacycle $[Pd^{II}(C_{12}H_8CO_2\text{-}C,O)L_2]$ (**B**). Structure **A** should be directly associated with the *cis*-$AnCO_2H$-*d* product. Structure **B** would yield a cis product only after a stereoselective endo protonolysis or a trans product after a selective exo protonolysis. Otherwise, a *cis*-/*trans*-$AnCO_2H$-*d* mixture should be expected. **C** should yield the 1:1 *cis*-/*trans*-$AnCO_2H$-*d* mixture.

the palladium−hydride bond (path a) is in agreement with the observed cis product. The subsequent steps, namely carbon monoxide insertion and hydrolysis of the resulting acylpalladium(II) complex, should not affect the configuration of the formerly olefinic carbon atoms. In the absence of side processes, the stereoselectivity of the whole reaction relies here solely on stereoselectivity of the metal hydride migratory insertion. A potential problem in this mechanism is that it requires the coexistence of a palladium hydride and acid in the reaction medium. Alternatively, the reaction can be thought to proceed via the (hydroxycarbonyl)palladium(II) complex (Scheme 1, path b). The insertion of the olefin into the palladium−carbon bond is expected to be cis, and in this approach the cis selectivity of the reaction depends on the selectivity of the subsequent protonolysis elimination step. The proton needs to attack the β-carbon from the side of the metal for the cis acid to be formed, and this raises some interesting questions. It is intriguing that very little or no trans acid is formed, since it would only require the appar-

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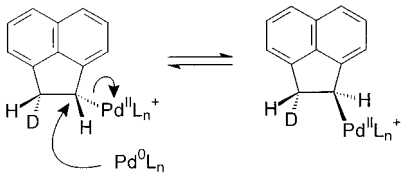
ently unhindered exo protonolysis, according to this route. We can speculate on the possibility of the protonation of the metal followed by cis reductive elimination to make this step compatible with overall cis selectivity, but we should be cautious at this point: while the protonation of *low-valent* metals is a feasible, well-documented reaction,[11] here we have a square-planar palladium(II) complex (formally a dication) that on protonation would become palladium(IV), a seemingly uncommon process altogether. After all, palladium(II) complexes are not characterized by their basicity and the oxidation state IV, unlike the case of platinum, is not a regular oxidation state for this metal and would be less so under reducing conditions. It would seem that route c, or the oxidative addition of Pd^0L_n to a carbocation formed by the protonation of the olefin, a mechanism proposed for carboxylations in strong acid media in particular[12] and in the older literature in general,[1d,13] would not explain the cis selectivity.

We have observed with L^F at 100 °C an exceptional case in which the single deuterium is incorporated nonselectively in both the cis and trans positions (Figure 2). Within Scheme 1, this immediately suggests alternative (b) coupled with unselective protonolysis or the carbocationic route (c), rather than (a) for the palladium alkyl formation. There is the possibility that the electronic nature of the phosphine and the reaction conditions could be crucial for the stability of intermediates **A** and **B**. Nevertheless, it should be pointed out that nonselective deuterium incorporation, as observed, is not entirely incompatible with hydride mechanism (a). A degenerate substitution equilibrium in which Pd^0L_n would attack the alkyl carbon with inversion could be operative; this process has been reported before for alkylpalladium species but, as far as we know, has never been observed in catalytic hydrocarboxylation:[14]



It should be stressed that very little or no deuterium is ever found in the H^c position, meaning that there is minimal or no α-carbonyl H/D exchange, and in so doing, the reaction meets an obvious prerequisite for the successful development of an enantioselective version. Also, because of the nature of the acenaphthenic ring system, C−C bond rotation is not possible and *β*-hydrogen (deuterium) elimination in the alkylpalladium complex would give a Pd−D species and leave no deuterium on the olefin (Scheme 1, path a);[15] this olefin is transparent to the *β*-elimination side process.

We have seen that acenaphthylene is a convenient substrate to establish the stereochemistry of the hydrocarboxy addition with a given catalytic system and have observed cis addition as required by a hydride intermediate. A hydroxycarbonyl intermediate will give a cis addition palladium intermediate as well, but in this case it is further required that it be followed by its stereoselective protonolysis. From a synthetic point of view, properly developed in terms of ligand tuning, catalytic hydrocarboxylation could become the preferred synthetic method to obtain $AnCO_2H$ and eventually other carboxylic acids: it is environmentally more benign than alternative preparations,[16] and its atom economy is good.

Experimental Section

General Considerations. Commercial technical acenaphthylene is of variable quality, containing acenaphthene (15−30%) and some tars. This acenaphthylene was recrystallized in pentane before use. Typically, the recrystallized material has an acenaphthylene content between 80 and 90%, the rest being acenaphthene and uncharacterized materials (2% by GC). Commercial $H_2C_2O_4{\cdot}2H_2O$ was used; deuterated oxalic acid ($D_2C_2O_4{\cdot}2D_2O$) was prepared by triple recrystallization with D_2O (60 °C/0 °C). Catalysis experiments were performed in a stainless steel custom-built pressure reactor (ca. 75 mL) of a standard vase and cover design, fitted with glass and fluorocarbon linings to avoid contact of the reacting solutions with the SS-316 steel reactor body. GC analysis was performed with twin HP G1800A chromatographs (HP-5 capillary columns, 0.25 mm diameter × 30 m), incorporating FID and MS detectors; decane was used as internal standard. NMR spectra are reported in the *δ* scale; ^1H and ^{13}C spectra are referenced to TMS, and the resonance of some added $CDCl_3$ was used to reference the ^2H spectra. All catalysis experiments have been duplicated. General conditions: 0.5 g of technical acenaphthylene (ca. 85%) in 10 mL of THF; $[PdCl_2(CH_3CN)_2] = 0.0066$ M (ca. 2%) plus *n* PAr_3 as specified in the tables; $[H_2ox{\cdot}2H_2O]/[Pd] = 50$; $P_{CO} = 30$ bar; time 24 h. Conversions over 40% in $AnCO_2H$ are isolated yields, which are within 5% of GC yields. Conversion values are corrected for true acenaphthylene content in each experiment. A protocol for the catalysis experiments is given below.

Model Catalytic Reaction Procedure (Table 2, Entry $[L^F]/[Pd] = 4$, Temperature 80 °C). The pressure reactor was charged with acenaphthylene (0.50 g, 85%, 2.8 mmol), $PdCl_2(CH_3CN)_2$ (0.017 g, 0.066 mmol), tris(*p*-fluorophenyl)-phosphine (0.083 g, 0.26 mmol), oxalic acid dihydrate (0.416 g, 3.3 mmol), and decane (50 *μ*L) dissolved in THF (10 mL). The reactor was purged and pressurized with CO. The mixture was heated to the reaction temperature and, after the gauge pressure was adjusted to 30 bar, stirred for 24 h at 80 °C. The reactor was then cooled, and its contents were transferred to a flask. The solvent was stripped off, the residue extracted with CH_2Cl_2 (ca. 15 mL), and the solution filtered. The acid product ($AnCO_2H$) was extracted as its sodium salt to a basic aqueous solution (3 × 10 mL, at pH 11−12). Under these conditions, the use of D_2O for the extractions did not cause the incorporation of any deuterium into the carboxylic acid. In independent blank experiments, incorporation of deuterium exclusively in the *c* position was observed only under much harsher conditions: i.e., with D_2O at pH 14 in 24 h. The aqueous layer was washed with fresh CH_2Cl_2 and acidified with HCl to precipitate the $AnCO_2H$ product, which can be recrystallized from toluene (yield 0.41 g, 74%). The remaining organic layer was concentrated and treated with hexanes; this

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caused the precipitation of the carbonylated oligomers, which were separated by filtration. Deuteriocarboxylation experiments were performed in the same way. Deuterium incorporation was in the range 60−80% (as measured by ^{1}H NMR), owing to the difficulty in adequately conditioning the reactor and the strong kinetic isotope effect that disfavors deuterium incorporation.

Data for $AnCO_2H$. ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.63 (1H, dd, H^a, $^2J_{ab}$ = 17.5 Hz, $^3J_{ac}$ = 8.7 Hz), 3.85 (1H, dd, H^b, $^3J_{bc}$ = 3.7 Hz), 4.60 (1H, dd, H^c), 7.2−7.8 (6H, m, arom H). ^{13}C NMR (62.5 MHz, $CDCl_3$, 298 K): δ 33.68 (*C*HD, *d* isotopomer, dt, J_{C-H} = 131.6 Hz, J_{C-D} = 20 Hz; C$_\beta$), 33.96 (*C*H$_2$, d_0 isotopomer, t, J_{C-H} = 132.5 Hz; C$_\beta$), 48.13 (*C*H, d, J_{C-H} = 133.5 Hz, C$_\alpha$), 119.71 (*C*H, d, J_{C-H} = 158.8 Hz), 120.64 (*C*H, d, J_{C-H} = 160.7 Hz), 123.44 (*C*H, d, J_{C-H} = 159.7 Hz), 124.14 (*C*H, d, J_{C-H} = 159.2 Hz), 127.84 (*C*H, d, J_{C-H} = 158.8 Hz), 127.96 (*C*H, d, J_{C-H} = 157.3 Hz), 131.53 (*C*, s), 138.10 (*C*, s), 141.35 (*C*, s), 142.82 (*C*, s), 179.22 (*C*O, s). IR (KBr, cm^{-1}): 1705 (ν_{CO}). Anal. Found (calcd) for $C_{13}H_{10}O_2$: C, 78.41 (78.77); H, 4.87 (5.08).

Data for the Polymers. Poly(acenaphthylene) was identified by comparison with a true sample; it was obtained as an ivory white powder with a melting range of 240−260 °C and M_w = 3000 (GPC-HPLC). Poly(acenaphthylene) is a commercial product, while $AnCO_2H$ to our knowledge is not. The carbonylated oligomer/polymer was isolated as a powder with a melting range of 140−160 °C; it is soluble in CH_2Cl_2, and GPC-HPLC showed it to be a mixture of two fractions, a heavier one with M_w = 4000 and a lighter one with M_w = 400. Spectroscopic data seem inconsistent with a possible *alt*-acenaphthylene−CO copolymer,[17] owing to its low carbonyl ^{13}C resonances δ_{CO} at 161 ppm, in both $CDCl_3$ and $(CF_3)_2CHOH$/$CDCl_3$ solvents. IR: ν_{CO} 1724 cm^{-1}.

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Supporting Information Available: NMR spectra of $AnCO_2H$ and IR and NMR spectra of the carbonylated oligomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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