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MECHANISM OF THE COPPER MEDIATED OXIDATION OF PRIMARY ALIPHATIC AMINES BY THE Cu^0 / O_2 / ACETIC ACID SYSTEM IN ACETONITRILE .

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Abstract : *Primary aliphatic amines are oxidized to aldehydes by the $Cu^0/O_2/$ AcOH system in acetonitrile . Kinetic measurements, particularly deuterium isotope effects studies, give support to the existence of a Cu(III) strong oxidant intermediate species in contrast with the Cu(I)/O_2/pyridine oxidant system in which Cu(II) has the major role.*

Numerous oxidizing reagents are known to convert primary aliphatic amines **1** (R = alkyl, aryl) either to aldehydes **3** (by oxidative deamination)[1,2] or to nitriles **4** (by dehydrogenation)[1-3], both via aldimines **2** :

$$\underset{\mathbf{1}}{R\text{-}CH_2\text{-}NH_2} \longrightarrow \underset{\mathbf{2}}{R\text{-}CH{=}NH} \longrightarrow \underset{\mathbf{3}}{R\text{-}CHO} \quad \text{or} \quad \underset{\mathbf{4}}{R\text{-}C{\equiv}N}$$

Limiting the subject to metallic reagents, the main oxidizing systems reported to yield aldehydes **3** are :

- the Cu^0/O_2 system, in water, which allowed Traube and Schönewald[4] to prepare acetaldehyde from ethylamine as early as 1906 and Demyanov and Shuikina[5] to obtain cyclanones from cyclopropyl and cyclobutyl amines .
- Fehling's solution (Cu^{2+}/ HO^-), generally unreactive toward aliphatic amines, readily oxidizes α-amino ketones to the corresponding α-dicarbonyl compounds[6] .
- The persulphate ($S_2O_8^{2-}$) / Ag(I) system transforms primary aliphatic amines, via highly reactive Ag(II) species[7].
- Other useful metallic reagents are manganese dioxide[8], potassium permanganate[9], baryum manganate[10], palladium dichloride and gold trichloride[11], Cr(VI) bipyridyl peroxide[12], potassium and baryum ferrates (FeO_4^{2-})[13,14] .

Nitriles **4** have also been prepared from primary amines by direct oxidation ; the metallic oxidizing reagents reported are nickel peroxide[15], lead tetraacetate[16,17], Cu(I) chloride / O_2 system in pyridine[18,19], and Ag(II) oxide[20] or picolinate[21] .

RESULTS

We have recently described in a synthetic communication[22] an improved and extended methodology for Kametani's oxidation of primary amines to nitriles[18] . By this procedure arylaliphatic amines (R = phenyl **1a** ; 4-MeO-C_6H_4 **1b** ; 3,4-$(MeO)_2C_6H_3$ **1c** ; 3,4-$(OCH_2O)C_6H_3$ **1d** ; 1-naphthyl **1e**) and aliphatic amines (R = n-propyl **1f** ; n-nonyl **1g** ; n-undecyl **1h**) are directly converted to the corresponding nitriles **4a-h**, in almost quantitative yields (96-99%) with very high purity :

$$\underset{\mathbf{1}}{R\text{-}CH_2\text{-}NH_2} + O_2 \xrightarrow[60°C,\ 24\ h]{Cu^{I}Cl\ (1.2\ equiv)/Pyridine} \underset{\mathbf{4}}{R\text{-}C{\equiv}N} + 2\ H_2O$$

The reaction seems to be catalyzed by Cu(I) : a turnover number of 5.5 with respect to Cu(I) in 24 hours reaction time is measured in piperonylamine **1d** oxidation but we have shown[23] that the early formed oxocopper (II) compound in Cu(I)Cl autoxidation in pyridine is responsible for these oxidations .

In order to explicit the mechanism of this reaction, the time course for the appearence of nitriles was monitored by glc in competition runs : plots of conversion percentage vs. time were determined for benzylamine **1a**/ veratrylamine **1c** and benzylamine **1a** / dodecylamine **1h** couples; the comparison of their initial slopes provides reactivities of dodecylamine / benzylamine / veratrylamine in the ratio 1/3.5/ 4.2 . Thus, neither the presence of a phenyl group nor methoxy electro-donating substituents on the phenyl have important kinetic implications ; the oxidation mechanisms of aliphatic and benzylic primary amines are likely of the same kind .
Plot of log [benzylamine] vs. time is linear, indicating that the oxidation reaction is first order with respect to benzylamine, for at least the first 90 minutes . The relative reactivities of benzylamine and its [α,α]-dideuteriated analogue are also measured by direct competition. Reaction is stopped before completion, unreacted amines are quantitatively acetylated by acetic anhydride, deuterium percentage is measured on the Ph-CH_2-NH-$COCH_3$ / Ph-CD_2-NH-$COCH_3$ product mixture by ^1H-NMR spectroscopy and used to calculate the deuterium isotope effect : k_H/k_D = 1.25 $\pm$ 0.1 (average value of 5 runs, at 50°C) which is typical of a secondary deuterium isotope effect, generally indicating that the C-H (or C-D) bond is not broken in the rate-determining step .

In this nearly unexplored field of primary aliphatic amines oxidation, the present paper deals with the mechanistic investigation of a novel Cu(I)/dioxygen oxidant system in weak acidic organic medium : benzylic primary amines **1a-e** are oxidized to benzaldehydes **3a-e** (55%) by molecular oxygen in acetonitrile, in the presence of excess (11 equiv.) of acetic acid and copper turnings (5 equiv), at 60°C :

$$\underset{\mathbf{1}}{Ar\text{-}CH_2\text{-}NH_2} \xrightarrow[CH_3CN\ /\ 60°C\ /\ 24h]{Cu^0/CH_3COOH/O_2} \underset{\mathbf{3}}{Ar\text{-}CHO} + Ar\text{-}CH_2\text{-}NH\text{-}COR'$$

5 : R' = H

6 : R' = CH_3

Two kinds of by-products are also isolated : N-benzyl formamides **5** (7%) and N-benzyl acetamides **6** (3%). The overall yield is 65%, neither starting nor tarry materials are recovered so 35% of starting material are thoroughly oxidized perhaps through hydroxylation and subsequent cleavage of aromatic moiety .

When oxidation of piperonylamine **1d** is carried out in the presence of propionic acid instead of acetic acid, piperonal **3d** (48%) and N-piperonylformamide **5d** (7%) are isolated but N-piperonyl-propionamide **6** (R' = C_2H_5) (3%) is found instead of the acetamide . The corresponding products, with the same overall (65%) and relative yields had been obtained in benzylamine **1a**, 4-methoxy benzylamine **1b**, 3,4-dimethoxybenzylamine **1c** and piperonylamine **1d** oxidations in presence of acetic acid .

It has been observed that copper turnings (slow corrosion) are much more efficient than copper powder (rapid corrosion) to promote amine oxidation (see below) .

Aliphatic amines (decylamine, dodecylamine) too are quantitatively oxidized in these experimental conditions but only unidentified polymers are isolated . In the reaction medium, enolizable aliphatic aldehydes and imines are polymerized via aldolization reactions .

On the other hand, neopentylamine **1i** gives non-enolizable pivalaldehyde **3i** (10% isolated as its 2,4-DNP derivative) :

$$\underset{\mathbf{1i}}{(CH_3)_3C\text{-}CH_2\text{-}NH_2} \xrightarrow[CH_3\text{-}CN\ /\ 60°C]{Cu^0\ /\ CH_3COOH\ /\ O_2} \underset{\mathbf{3i}}{(CH_3)_3C\text{-}CHO}$$

Kinetics :

Benzylamine **1a** and veratrylamine **1c** equimolar mixtures are oxidized in the above-mentioned experimental conditions ($Cu^0/O_2/CH_3COOH$ in acetonitrile at 50°C), the time course for the appearance of products (benzaldehyde and veratraldehyde) can be conveniently monitored by gas-liquid chromatography . Comparison of the initial slopes of the plots of conversion percentage vs time, indicate that their oxidation rates are quite identical within experimental errors . The presence of two methoxy electron-donating groups on the aromatic moiety is of no kinetic consequence .

Deuterium isotope effect :

Piperonylamine **1d** has been choosen for practical reasons : on one hand the product stability

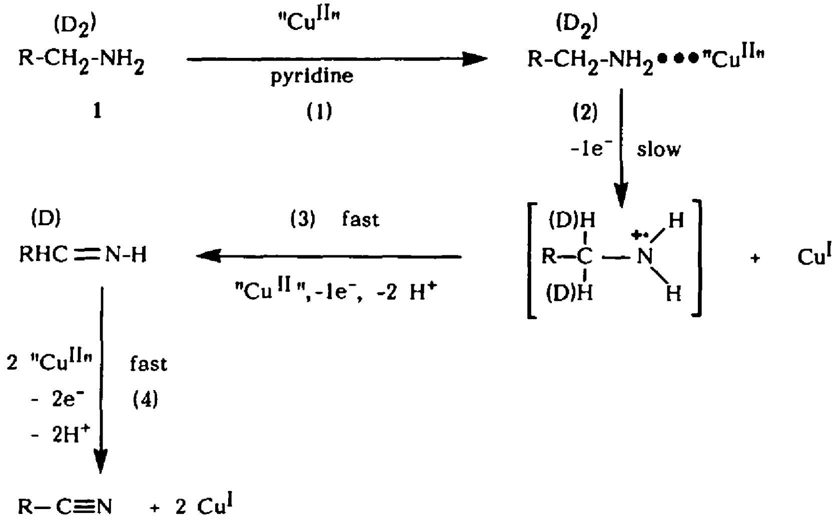
(piperonaldehyde is resistant to autoxidation), on the other hand the accuracy of the aldehydes NMR spectra integrations .
A mixture of piperonylamine and its (α,α)-dideuteriated analogue is oxidized in the forementioned acidic medium . The reaction is stopped before completion, unreacted amines are separated by acid extraction and deuterium percentage is determined by ^1H-NMR on the purified mixture of products : 3,4-$(OCH_2O)C_6H_3$-CHO / 3,4-$(OCH_2O)C_6H_3$-CDO .
This oxidation is first order with respect to piperonylamine for at least the first 90 minutes (plot of log [amine] vs. time is linear) ; oxidation rate constants ratio is easily calculated : $k_H/k_D = 3.6 \pm 0.1$ (temperature = 50°C, average value of 3 runs) . This value is typical of a primary deuterium isotope effect, indicating that the C-H (or C-D) bond is cleaved in the rate-determining step in contrast with the forementioned oxidation in basic medium .

DISCUSSION, MECHANISM

Thus, primary amines are oxidized by oxygen, in the presence of different Cu(I)/dioxygen systems either in basic or weakly acidic medium ; kinetic and deuterium isotope effects data allow to propose in each case a specific mechanism (scheme 1 and 3) .

Oxidation in pyridine :

We have recently shown[23] that the early formed oxocopper(II) compound in Cu(I)Cl/O_2/pyridine system : $(pyridine)_4Cu_4Cl_4O_2$ (with $-Cu^{II}-O-Cu^{II}-$ i.e. μ-oxo patterns), extensively studied by Davies and coworkers[24], is an exceptionally strong oxidant, responsible for amine four-electron oxidation to nitriles .
On scheme 1, a mechanism is proposed to account for kinetic data ; it seems reasonable to admit that the first step is a classical[25] complexation of Cu(II) salts with amines, "Cu^{II}" represents the oxocopper(II) oxidizing complex .
The results obtained are consistent with step 2 being electron-transfer from amine to "Cu^{II}" species and providing Cu(I) and an aminium radical. This step is likely a slow, rate-determining process ; although C-H or C-D bonds are not cleaved in the transition state, the observed secondary isotope effect ($k_H/k_D = 1.25$) is quite consistent with differences in nitrogen charge stabilization by hyperconjugation between C-H and C-D[26,27]. Similar deuterium isotope effect ($k_H/k_D = 1.3$) and mechanism have been reported[28,29] in the oxidative dealkylation of N,N-dimethylbenzylamine ($Ph-CH_2-N(CH_3)_2$ / $Ph-CD_2-N(CH_3)_2$) by iodosylbenzene, catalyzed by Fe(III) or Mn(III) porphyrins.
To explain the small but significant rate enhancement from dodecylamine to benzylamine and veratrylamine, the increasing stabilization of the charged aminium species by electron-donating groups may be invoked .



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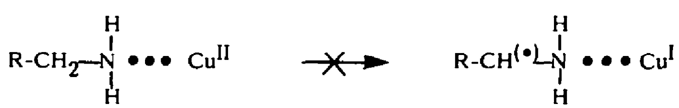
Scheme 1

Proposed mechanism for primary amine oxidation by oxocopper(II) species .

Furthermore, these kinetic and isotope effect studies allows to reject a mechanism where a H• abstraction step would be rate-determining :



primary isotope effect (ranging from 2.8 to 7)[28] and an important increase of the rate from R = alkyl to R = aryl would have been observed .

Release of an α-proton (step 3) from the aminium radical is known to be a fast reaction[28] that would be strongly catalyzed by the basic solvent (scheme 1). An imine is then formed which is readily oxidized to nitrile (step 4) in very fast classical[30-32] reactions with Cu(II) salts :

$$\text{R-CH=NH} + 2\ \text{Cu}^{II} + 2\ \text{B (base)} \xrightarrow{\text{fast}} \text{R-C}\equiv\text{N} + 2\ \text{Cu}^{I} + 2\ \text{BH}(+)$$

Cu(II) concentration should be large enough to insure a very fast imine oxidation to nitrile and prevent the competitive starting material addition on imine :

$$\text{R-CH=NH} + \text{R-CH}_2\text{-NH}_2 \longrightarrow \underset{\mathbf{7}}{\text{R-CH=N-CH}_2\text{-R}} + \text{NH}_3$$

otherwise, hydrolysis of ketimine **7** would occur during the work-up and provide aldehyde **3** and recovered starting material **1**[23] .

It should be emphasized that Cu(I) is reactivated in steps 2,3 and 4 ; thus catalytic conditions are obtained under a dioxygen atmosphere .

Oxidation in acidic organic medium :

The primary isotope effect measured in organic acid solution obviously requires a different mechanism in which α C-H bond cleavage is rate-determining .

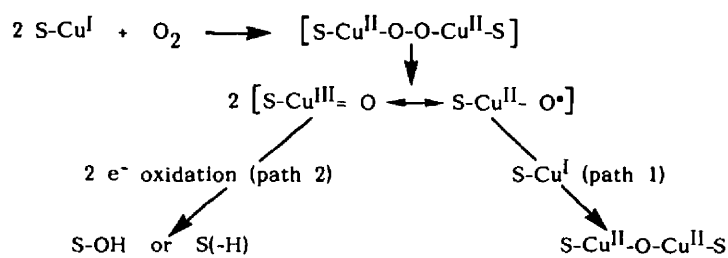
As early as 1856 ammonia oxidation to nitrite ion (NO_2^-) by the Cu^0/O_2 system in water was reported[33] and oxidation of aliphatic primary amines by the same system appeared in the beginning of the century[4].

Copper corrosion by carboxylic acids in non aqueous solutions and in the presence of dioxygen was also reported[34,35].

In our oxidizing system (Cu^0/ O_2 / CH_3-COOH in acetonitrile) it is necessary to use copper turnings (slow corrosion reaction) rather than copper powder (fast corrosion) in order to obtain fair conversion percentage . The Cu(I)/O_2 oxidizing system is likely formed by metallic copper corrosion :

$$2\ Cu^0 + 2\ Ac\text{-}OH + 1/2\ O_2 \longrightarrow 2\ Cu^I\text{-}OAc + H_2O$$

In previous mechanistic studies concerning phenols[36], alcohols[37,39], and carboxylic acids[35] oxidations by Cu(I)/O_2 systems, in acetonitrile, we have postulated[35-39] that an early formed μ-peroxodicopper(II) intermediate homolytically cleaves to reactive Cu(III) oxo species bound to the organic hydroxylic substrate S-H (cupryl S-Cu^{III}= O) which either reacts with a cuprous entity S-Cu(I), especially with large Cu(I) concentrations (path 1) to provide μ-oxo Cu(II) compounds[35,37] or afford a two-electron redox reaction (path 2) responsible for hydroxylation or dehydrogenation reactions of the substrate ligand ; these sequences are summarized by scheme 2 :

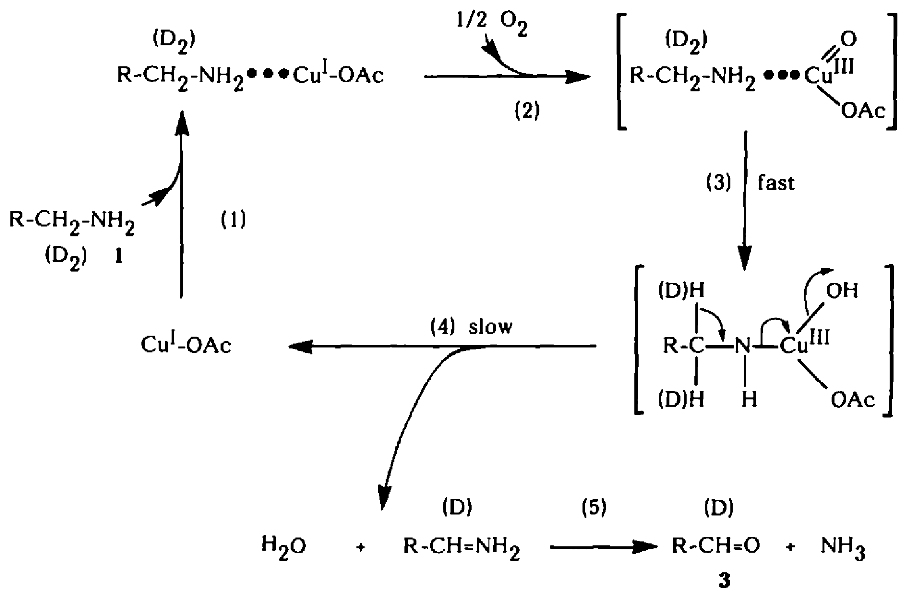


Scheme 2

According to this scheme, in contrast to the slow corrosion of copper turnings that provides very low Cu(I) concentration and favored path 2, Cu^0 powder corrosion gives high Cu(I) concentration.

so path 1 will be the major way, where μ-oxo Cu(II) species is protonated to provide the quite unreactive Cu(II) acetate . Furthermore it has long been reported[41] that Cu(I) chloride - primary aliphatic amine complexes react with dioxygen to afford Cu(II) complexes without any ligand oxidation.

In the proposed mechanism (scheme 3), it is reasonable to admit that the first step consists in classical Cu(I) salt complexation with amine[41] . Step 2 represents the above-mentioned (scheme 2) reaction of Cu(I) entities with O_2 to provide reactive two-electron oxidant cupryl species . Step 3 consists in the nitrogen-Cu(III) bond formation with concomitant migration of nitrogen proton to Cu(III) oxygen ligand . Such N-deprotonations have been already observed in the case of stable complexes involving amino nitrogen-Cu(III) bonds[42]. The following carbon-deprotonation is likely a slow and spontaneous reaction (step 4), the observed primary deuterium isotope effect (k_H/k_D = 3.6) reflects this rate-determining step where α C-H (or C-D) bond is broken with a concomitant two-electron oxidation of amino ligand to an imine and reduction of Cu(III) to Cu(I). In these conditions the produced water readily hydrolyses imines (step 5) to aldehydes **3** .



Scheme 3

Mechanism for primary amine oxidation by the Cu^I/O_2 system .

Benzylamine and veratrylamine have the same oxidation rate ; this result rules out an intramolecular electron transfer mechanism involving the aromatic nucleus :

$$Ar\text{-}CH_2\text{-}\overset{+}{N}H_2\text{-}Cu^{III}(OAc)(OH) \not\rightleftarrows Ar(^{+\cdot})\text{-}CH_2\text{-}\overset{+}{N}H_2\text{-}Cu^{II}(OH)\ AcO^- \rightarrow \cdots$$

analogous to the mechanism reported[43] by Jönsson in arylacetic acids oxidation by Cu(III) in acid solution, because methoxy substituted benzylamines should have very fast transformation rates compared to unsubstituted benzylamine .

The acetamide **6** by-product occurence may be explained by the classical amine reaction with acetic acid in similar conditions . A possibility to account for formamide **5** may be a similar reaction with formic acid formed in the further oxidations of products but evidences are not yet available .

EXPERIMENTAL

1) General :

All reagents are commercially available, except deuteriated piperonylamine ; primary amines are used without further purification . Acetonitrile is dried over $CaCl_2$ and distilled on P_2O_5 . Melting points were determined on a Kofler (Reichert) apparatus . α-dideuteriated piperonylamine is classically prepared[44] by reduction of piperonylonitrile **4d** in tetrahydrofuran by $LiAlD_4$.

2) Primary amine oxidation in acid medium :

a) Typical procedure :
To a solution of 1 g (6,62 mmol) of piperonylamine **1d** in 100 ml acetonitrile, 4.2 ml (11 equiv) acetic acid and 2.1 g (5 equiv) copper turnings are added, the mixture is stirred in an oxygen atmosphere for 24 h at 60°C. The solvent is distilled in vacuo, the slurry treated with 50 ml 5% HCl, then extracted with ethyl acetate (4 x 50 ml) . The extracts are dried on $MgSO_4$, decolorized on activated carbon and filtered, the solvent is removed under reduced pressure to afford 0.760 g of crude product from which piperonal **3d**, 0.520 g (52%), mp 35-36° (lit.[45] mp 37°), N-piperonylformamide 0.083 g (7%) and N-piperonylacetamide 0.038 g (3%) are separated by preparative thin layer chromatography (silica gel, CH_2Cl_2 : cyclohexane, 75 : 25) and compared with authentic samples .

b) Kinetic study :
To a solution of 0.679 g (6.34 mmol) benzylamine **1a**, 1.059 g (6.34 mmol) veratrylamine **1c** and 0.422 g (3.17 mmol) 4-methoxy benzonitrile **4b** (as an unreactive internal standard) in 120 ml anhydrous acetonitrile, 8 ml (11 equiv) acetic acid and 4 g (5equiv) copper turnings are added . The mixture is stirred in an oxygen atmosphere for 8 h at 50°C . The reaction is followed by transferring 1.5 ml of mixture at regular intervals (15 mn during the 3 first hours, then 30 mn) in 2.5 ml 10% HCl . Extraction with ether (2 x 2 ml), drying over $MgSO_4$ give samples from which kinetics were monitored by following aldehydes appearance by glc (OV 25 on AW-DMC 80/100 Chromosorb, 2 m, Ø 1/8", temp.: 80° to 240°C (10°C/mn), N_2: 20 ml/mn) . Plots of conversion percentage vs. time are identical for benzaldehyde and veratraldehyde (initial slopes are the same) indicating that benzylamine has the same oxidation rate in this system as veratrylamine within experimental errors .

c) Isotope effect :
A mixture is prepared with 1.572 g (10.4 mmol) piperonylamine **1d** and 1.860 g (12.1 mmol) dideuteriated piperonylamine (respectively 45.4% and 54.6% by ^1H NMR accurate integration) In each oxidation run, 0.400 g of mixture is dissolved in 50 ml CH_3CN with 1.7 ml (11 equiv) AcOH and 0.84 g (5 equiv) Cu turnings, for example, in run 1, the mixture is stirred in an oxygen atmosphere at 50°C, the reaction is stopped before completion (90 mn) , the solvent evaporated under reduced pressure, the residue is taken up with 50 ml ethyl acetate and filtered on silicagel (230-400 mesh), the crude product (0.180 g) is chromatographed (preparative tlc, on silicagel, dichloromethane : cyclohexane (80:20); a mixture is isolated (0.090 g) . Piperonal and piperonal-d are readily evaluated by NMR spectrum integration of aldehyde proton at 9.80 ppm and methylenedioxy (-O-CH_2O-) protons at 6.0 ppm : 71.8% and 28.2% piperonal / piperonal-d .

Rate constants ratio is described by the following equation :

$$\frac{k_H}{k_D} = \frac{\log\left[1 - (H)_f/(H)_i\right]}{\log\left[1 - (D)_f/(D)_i\right]}$$

with $(H)_i$ and $(D)_i$ = initial molarities of piperonylamine and deuteriated piperonylamine ; $(H)_f$ and $(D)_f$ = measured molarities of the products (piperonal and piperonal-d) .
The calculated value is 3.54 . Two other runs (with reaction time of 45 mn and 60 mn) provide close values (respectively 3.62 and 3.71); the average value is : $k_H/k_D = 3.6 \pm 0.1$.

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