*Journal of Organometallic Chemistry*, 269 (1984) 115–121
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

# REACTIONS OF ORGANOMERCURY FULMINATES WITH ACETYLENE DERIVATIVES

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(Received February 22nd, 1984)

## Summary

Organomercury fulminates react with acetylene derivatives to give unstable 3-(organomercurio)isoxazoles, which isomerize to 2-cyanoenolates. These are hydrolyzed with hydrochloric acid to the corresponding enols and are cleaved by water at the double bond. With monosubstituted acetylenes, substitution at the free position by the organomercury residue is predominant.

## Introduction

Analogies and differences between trimethylsilanecarbonitrile oxide (Ia) and organic nitrile oxides have been previously pointed out [1,2,3]. Thus, cycloaddition reactions are a common feature, although the silylated cyclo-adducts easily rearrange to open-chain products (e.g. the cyano silyl ether IVa) [2]. However the silylated compound Ia is stable as a monomer, by contrast with organic nitrile oxides.

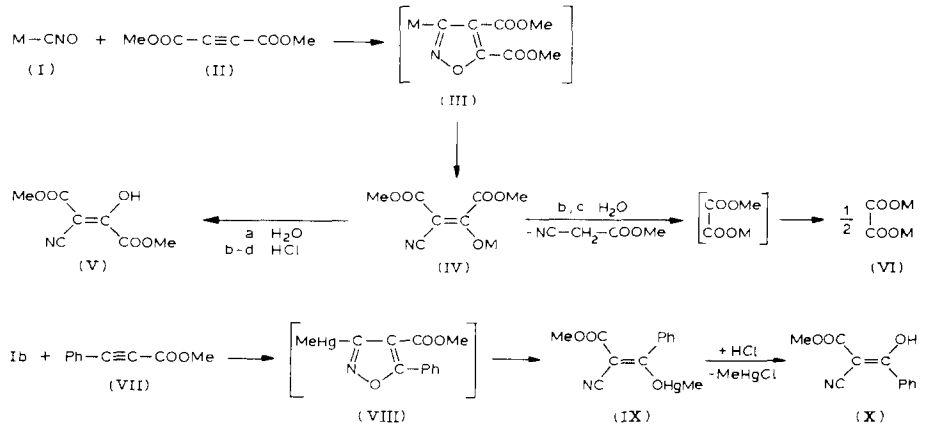
These studies are now extended to organomercury fulminates (Ib–Id): they have been known for many years [4,5], but only reactions with inorganic reagents have previously been reported [6].

## Results and discussion

On treatment with dimethyl acetylenedicarboxylate (II), the fulminate Ib gives an isolable adduct, whose structure IVb is supported by the IR, Raman and UV spectra in the solid state, indicating the presence of C≡N and C=C bonds. Similar reactions (Scheme 1) were carried out on dimethyl acetylenedicarboxylate (II) with the fulminates Ic and Id, and on methyl phenylpropiolate (VII), with the fulminate Ib: the adduct IVc could be isolated, but evidence for the adducts IVd and IX was only obtained in solution. Only one regioisomer (VIII) was produced by addition of the fulminate Ib to the ester VII, identified by comparison of the hydrolysis product (X) with an authentic sample of methyl benzoylcyanoacetate.

0022-328X/84/$03.00 

SCHEME 1. a, M = $Me_3Si$; b, M = MeHg; c, M = PhHg; d, M = ONC–Hg



The $^{13}C$ NMR data (DMSO solutions) of the adducts IV and IX are collected in Table 1: the spectra of the adducts IVb–IVd are almost identical, but markedly different from the reported spectrum of the silyl ether IVa in deuteriochloroform [2]. A comparison with dimethyl cyanohydroxyfumarate (V), or better with its K-salt, suggests that the adducts are considerably dissociated in DMSO.

The mercurated compounds IVb–IVd are less sensitive to solvolysis than the parent compound IVa: conversion into the corresponding enol (V) is achieved rapidly by atmospheric moisture for IVa, but requires more acidic conditions on the others (e.g. aqueous HCl). With water, the organomercury enolates IVb–IVc decompose slowly, with cleavage of the C=C bond, according to Scheme 1: methyl cyanoacetate is identified in the solutions, while the products VIb, VIc separate slowly. These are identified as bis(organomercury) oxalates on the basis of analytical and spectral data and because of their conversion into dimethyl oxalate by treatment with hydrochloric acid in methanol. The oxalates VIb, VIc are presumably produced via the intermediate methyl organomercury oxalates.

Moreover, the organomercury enolates IVb–IVd are stable towards dimethylsulfoxide at room temperature, whereas the silyl enolate IVa is cleaved in these

TABLE 1

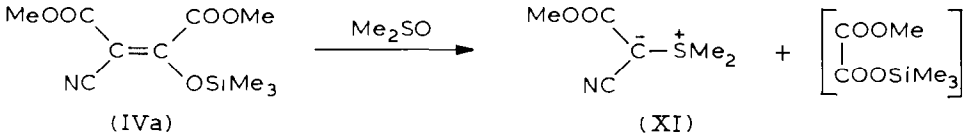
$^{13}C$ NMR CHEMICAL SHIFTS

| Compound | Solvent | *C*N | =*C*(CN) | =*C*(O) | O=*C*–O | O–*C*$H_3$ |
|---|---|---|---|---|---|---|
| IVa | $CDCl_3$ [a] | 112.1 | 90.8 | 166.8 | 162.3, 161.7 | 52.8, 52.3 |
| IVa | DMSO-$d_6$ [b] | 119.8 | 72.0 | 180.6 | 167.6, 167.2 | 51.4, 50.2 |
| IVb | DMSO-$d_6$ | 121.5 | 70.0 | 182.0 | 168.1, 167.6 | 51.4, 50.2 |
| IVc | DMSO-$d_6$ | 121.1 | 69.8 | 181.9 | 168.0, 167.5 | 51.1, 50.0 |
| IVd | DMSO-$d_6$ [c] | 121.2 | 70.2 | 181.9 | 168.0, 167.6 | 51.3, 50.1 |
| V | $CDCl_3$ [d] | 111.9 | 85.2 | 169.1 | 169.9, 159.2 | 54.0, 53.7 |
| V | DMSO-$d_6$ | 119.0 | 74.1 | 179.7 | 167.1, 166.8 | 52.4, 51.3 |
| V,K-salt | DMSO-$d_6$ [e] | 121.0 | 71.2 | 182.6 | 168 8, 168.4 | 52.1, 50.9 |
| IX | DMSO-$d_6$ | 121.8 | 75.7 | 187.4 | 167.6 | 50.9 |

[a] Ref. 2. [b] Evolution to the ylide XI-$d_6$ is complete in several h. [c] Containing residual THF. [d] Ref. 1. [e] Containing ca. 13% water.

conditions to give the sulfonium ylide (XI) in excellent yield (Scheme 2). The last

SCHEME 2

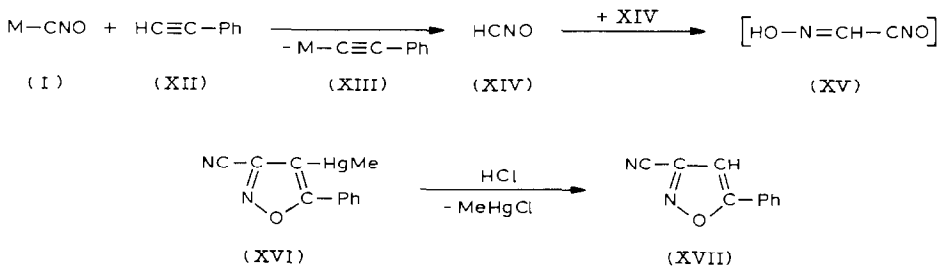



(IVa) (XI)

reaction appears to require strong electron-withdrawal, as the trimethylsilyl enol ethers derived from acetophenone, dibenzoylmethane and benzoylacetonitrile did not react with dimethyl sulfoxide.

With phenylacetylene (XII), either the fulminates Ia and Ib lead to substitution at the free acetylenic position, according to the equation illustrated (Scheme 3).

SCHEME 3. a, M = $Me_3Si$; b, M = MeHg.




Therefore, several different cycloadditions can, in principle, take place at the same time, between either dipolarophile XII or XIII and one of the dipoles I, XIV or XV. It follows that different products are obtained, according to the relative formation rates. Thus, from methylmercury fulminate (Ib) and phenylacetylene (XII) the substituted phenylacetylene (XIIIb) was the main product; in addition, the mercurated isoxazole (XVI) was isolated, possibly arising from the substituted phenylacetylene (XIIIb) and the dimer of fulminic acid (XV). The mercurated isoxazole (XVI) was easily hydrolysed to the known 3-cyano-5-phenylisoxazole (XVII), identified by an IR comparison with an authentic sample [7].

From trimethylsilanecarbonitrile oxide (Ia) and phenylacetylene (XII), the main products were 3-[(trimethylsilyl)oxy]cinnamonitrile (rearranged Ia + XII), 5-phenylisoxazole (XIV + XII) and trimethylsilylphenylacetylene (XIIIa), as already reported [2].

## Experimental

Melting points were determined on a RCH Kofler apparatus. Vacuum distillations were carried out by a Büchi GKR-50 Kugelrohr distillator. Microanalyses were carried out with a Perkin–Elmer 240C elemental analyzer, equipped with a gold trap for mercury-containing compounds. Column chromatographies (silica gel) were carried out under nitrogen pressure, using a Jobin–Yvon Chromatospak Prep-10 apparatus. Gas-chromatographic analyses were made with a Carlo Erba 4200 instrument. Mass spectra were recorded on a LKB 2091 mass spectrometer by GC

inlet, unless otherwise stated. IR spectra were obtained with a Perkin–Elmer 283 and UV spectra with a Cary 14 spectrophotometers. NMR spectra were recorded on Perkin–Elmer R 32 ($^1$H, 90 MHz, CW) and on Varian FT-80 A ($^{13}$C, 20 MHz; $^{199}$Hg, 14.176 MHz) spectrometers, in DMSO solutions unless otherwise indicated: the chemical shifts are given in ppm from TMS ($^1$H and $^{13}$C) or from neat dimethylmercury ($^{199}$Hg); coupling constants ($J$) are in Hz.

Dimethyl acetylenedicarboxylate, phenylacetylene and methyl propiolate were purchased from Fluka. Methyl phenylpropiolate was obtained by esterification of the acid, prepared as described in ref. 8.

*Methylmercury fulminate (Ib)*

Mercury fulminate (ca. 10 g) was treated under stirring with a boiling solution of dimethylmercury [9] in anhydrous THF (200 ml) during 1 h. After removal of the solvent in vacuo, the solid residue was extracted with hot acetone (300 ml), the solvent removed and the solid residue crystallized from chloroform to give needles, m.p. 139–141 °C, dec., (reported [5] m.p. 146 °C, dec., from cyclohexane), yield 50%. IR (KBr): 2220 cm$^{-1}$. NMR data are reported elsewhere [10].

*Phenylmercury fulminate (Ic)*

The reported procedure, starting from mercury fulminate and phenylmagnesium bromide [4], was modified by carrying out the reaction in THF at room temperature rather than in boiling diethyl ether. Yield 68%, m.p. 175–177 °C, dec. (from methanol at −70 °C); reported [4] m.p. 178 °C, dec. (from acetone-water). IR (KBr): 2220 cm$^{-1}$. NMR data are reported elsewhere [10].

*Dimethyl cyano[(methylmercury)oxy]maleate (IVb)*

A solution of methylmercury fulminate (Ib, 1g, 3.88 mmol) and dimethyl acetylenedicarboxylate (0.51 ml, 4.15 mmol) in anhydrous benzene (15 ml) was refluxed during 10 min. After cooling, the precipitated product (IVb) was collected, washed with anhydrous diethyl ether and dried: m.p. 173–177 °C, dec., yield 82%. Needles, m.p. 180–181 °C, dec. (from toluene). Found: C, 24.08; H, 2.25; N, 3.43. $C_8H_9HgNO_5$ calcd.: C, 24.04; H, 2.27; N, 3.50%. IR (KBr): 2200, 1755, 1705, 1560 cm$^{-1}$, all strong; Raman (solid, cm$^{-1}$): 2217m, 1729w, 1674m, 1578vs; UV (Nujol mull): $\lambda_{max}$ 278 nm. $^1$H NMR: 0.83, 3.40 and 3.53 (all singlets). $^{13}$C NMR: see Table 1. $^{199}$Hg NMR: −1096. *m/z*: 401 (1%, $M^+$), 342 (44, $M^+ - COOMe$), 140 (55, $M^+ - COOMe - Hg$), 126 (100, $M^+ - COOMe - CH_2Hg$), 96 (20), 94 (22), 82 (28), 59 (91, $COOMe^+$), 58 (40).

*Hydrolysis of IVb*

A solution of IVb in pure chloroform was stirred with water for 5 h. Methyl cyanoacetate was identified in the organic solution by comparison (GC, MS, $^{13}$C NMR) with a commercial sample; two additional $^1$H NMR signals ($\delta$ 1.23, 3.85) were assigned to methyl methylmercury oxalate. A solid, which separated slowly from the solution as white leaves, was collected in 66% yield (m.p. 275 °C, dec.) and identified as bis(methylmercury) oxalate (VIb) on spectral and chemical grounds. Found: C, 9.21; H, 1.06. $(C_2H_3HgO_2)_2$ calcd.: C, 9.25; H, 1.16%. IR (KBr): 1600 cm$^{-1}$, broad. $^1$H NMR: 0.75. $^{13}$C NMR: −0.7q, 167.1s. $^{199}$Hg NMR: −1094. *m/z* (direct inlet): 232 (15%, $CH_2HgO^+$), 217 (71, $MeHg^+$), 202 (63, $Hg^+$), 44 (100,

$CO_2^+$). A suspension of this product in methanol gave, on treatment with dry HCl, dimethyl oxalate, identified by a GC comparison with an authentic sample.

*Dimethyl cyano[(phenylmercury)oxy]maleate (IVc)*

A solution of phenylmercury fulminate (Ic, 0.8 g, 2.5 mmol) and dimethyl acetylenedicarboxylate (0.32 ml, 2.6 mmol) in anhydrous benzene (50 ml) was refluxed for 3 h. The solution was cooled, filtered, and the solvent was removed in vacuo from the clear solution. The solid residue was washed with diethyl ether and dried: m.p. 142–144°C, dec., yield 57%. Found: C, 34.13; H, 2.46; N, 2.88. $C_{13}H_{11}HgNO_5$ calcd.: C, 33.81; H, 2.40; N, 3.03%. IR (KBr): 2200s, 1754m, 1700vs, 1560vs $cm^{-1}$. $^1H$ NMR: 3.02s, 3.85s, 7.4–7.5m. $^{13}C$ NMR: see Table 1. $^{199}Hg$ NMR: −1427.

*Hydrolysis of IVc*

Under the same conditions as described for IVb, bis(phenylmercury) oxalate (VIc) was collected (60%), m.p. 255°C, dec. Precipitated twice from DMSO with water, m.p. 257°C, dec. Found: C, 25.58; H, 1.34. $C_{14}H_{10}Hg_2O_4$ calcd.: C, 26.13; H, 1.57%. IR (KBr): 1635 br $cm^{-1}$. $^1H$ NMR: 7.3–7.6m. $^{13}C$ NMR: 128.1d, 128.4d, 137.0d and 146.1s (Ph), 168.4s (CO). $^{199}Hg$ NMR: −1426br. This oxalate (VIc) was converted into dimethyl oxalate by the procedure employed for the oxalate (VIb).

*Dimethyl cyano[(fulmidomercury)oxy]maleate (IVd)*

Mercury fulminate (ca. 6 g) was treated under stirring with a solution of 1 equiv. of dimethyl acetylenedicarboxylate (2.6 ml) in anhydrous THF (30 ml). After 24 h, the mixture was centrifuged and the clear solution stored in refrigerator. Attempts to isolate the adduct IVd were unsuccessful. A sample of the solution was added to DMSO-$d_6$, most of the THF was removed in vacuo, and the NMR spectra recorded on the residual solution: $^1H$, 3.45s, 3.60s. $^{13}C$, see Table 1.

*Acid hydrolysis of the adducts IV: dimethyl cyanohydroxyfumarate (V)*

A chloroform solution (5%) of the adduct IVb was stirred with 0.1 vol. of conc. HCl. The residue obtained upon concentration of the dried organic layer was column-chromatographed (silica gel, eluant chloroform) to afford methylmercury chloride followed by the ester V.

A 5% chloroform solution of IVc was stirred with 0.1 vol. of conc. HCl and the precipitated phenylmercury chloride collected (90%). The organic layer was dried and concentrated, the residue dissolved in tetrachloromethane to remove more chloride (4%): this solution gave, on concentration, the ester V, m.p. 106–111°C (reported [11] m.p. 108°C), yield 95%.

A solution of the adduct IVd in THF, obtained as above, was treated with 0.1 vol. of conc. HCl and the organic layer concentrated in vacuo. The residual oil was extracted at room temperature with $CCl_4$ to give, on solvent removal, the crude product V, 1.9 g m.p. 98°C, recrystallized, m.p. 111°C (from benzene).

*Methyl 2-cyano-3-[(methylmercury)oxy]cinnamate (IX)*

A solution of equivalent amounts of methylmercury fulminate (Ib) and methyl phenylpropiolate (VII) in anhydrous benzene (0.5 *M*) was refluxed for 7 h. The solvent was removed in vacuo, but the residual oil (crude IX) could not be distilled without decomposition. $^1H$ NMR (benzene): 0.5s, 3.45s. $^{13}C$ NMR: see Table 1.

*Acid hydrolysis of the adduct IX: methyl benzoylcyanoacetate (X)*

The solution of IX in benzene, obtained as above, was cooled and treated under stirring with 0.25 vol. of conc. HCl. The organic layer was separated and extracted with 10% aqueous sodium carbonate. On acidification of the aqueous extract, the ester X precipitated: m.p. 75–77 °C (from ethanol), yield 51% (with respect to Ib), identified by comparison with an authentic sample [12].

*Dimethylsulfonium carboxycyanomethylide, methyl ester (XI)*

The silyl enolate IVa [2] (2.5 g, 9.7 mmol) was treated under nitrogen with anhydrous DMSO (2 ml, 28.2 mmol) overnight. The precipitated ylide XI was collected, washed with diethyl ether and dried. Yield 1.26 g (81%), m.p. 152–153 °C; reported m.p. 158–160 °C (from acetone/ether) [13]. IR and $^1$H NMR spectra in agreement with the literature [13]. $^{13}$C NMR ($CDCl_3$): 167.4s (O=C–O), 118.6s (CN), 50.9q ($OCH_3$), 36.2s (C–S), 29.2q ($SCH_3$). *m/z* (direct inlet): 159 (67%, $M^+$), 144 (100, $M^+ - Me$), 128 (47, $M^+ - MeO$), 116 (16), 112 (26), 85 (44, $M^+ - Me - COOMe$), 84 (16), 70 (36), 62 (40, $Me_2S^+$), 61 (16), 59 (28, $COOMe^+$), 47 (22, $MeS^+$), 46 (11), 45 (35), 44 (15).

*Reaction of Ib with phenylacetylene: 3-cyano-4-methylmercurio-5-phenylisoxazole (XVI)*

A solution of methylmercury fulminate (Ib, 1.5 g, 5.8 mmol) and phenylacetylene (XII, 0.68 ml, 5.8 mmol) in anhydrous benzene (30 ml) was refluxed for 4.5 h. After removal of solid impurities, the solution was concentrated in vacuo and the residue chromatographed (eluant: chloroform + light petroleum, 2 : 1). The following main components were collected sequentially: XIIIb (0.91 g, 50%), XVII (17 mg), XVI (0.225 g, 10%).

*1-Methylmercury-2-phenylacetylene (XIIIb).* Crude m.p. 41 °C; after Kugelrohr distillation (oven *t* 130–135 °C and 0.04 Torr), m.p. 43–44 °C, 0.71 g; reported [14] b.p. 97–105 °C at 0.7 Torr. Found: C, 33.99; H, 2.48. $C_9H_8Hg$ calcd.: C, 34.44; H, 2.54%. IR (KBr): 2130 $cm^{-1}$. $^1$H NMR: 0.44s (3H), 7.15–7.5m (5H). $^{13}$C NMR: 143.1 and 104.4 (both s, C≡C), 131.4d, 128.5d, 127.6d and 124.0s (Ph), 6.7q (Me). $^{199}$Hg NMR: −542q, $J(^{199}Hg–^1H)$ 154.7. A sample of XIIIb in methylene chloride was stirred for 3 min with conc. HCl and the organic layer washed with water: the organic solution contained phenylacetylene (XII, identified by GC) and methylmercury chloride (isolated by concentration and washing with light petroleum: m.p. 172–173 °C, IR comparison).

*3-Cyano-4-methylmercury-5-phenylisoxazole (XVI).* Crude m.p. 113–114 °C; recrystallized from ligroin (b.p. 80–120 °C), 0.19g, m.p. 113–115 °C. Found: C, 34.50; H, 1.99; N, 7.03. $C_{11}H_8HgN_2O$ calcd.: C, 34.33; H, 2.09; N, 7.27%. IR (KBr): 2250 $cm^{-1}$. $^1$H NMR ($CDCl_3$): 0.92s (3H), 7.5–8.0m (5H). $^{13}$C NMR ($CDCl_3$): 178.3s, 150.3s and 145.0s (isoxazole ring), 130.8d, 129.1d, 127.8s and 125.9d (Ph), 112.6s (CN), 11.6q (Me). $^{199}$Hg NMR ($CDCl_3$): −344q, $J(^{199}Hg–^1H)$ 138. *m/z*: 386 (49%, $M^+$), 371 (2, $M^+ - Me$), 356 (59, $M^+ - NO$), 170 (3, $M^+ - HgCH_2$), 154 (31, $M^+ - NO - Hg$), 139 (100, $M^+ - NO - HgMe$), 127 (8), 113 (12), 105 (28, $PhCO^+$), 89 (18), 77 (56, $Ph^+$). A chloroform solution of XVI was refluxed for 0.5 h with dil. HCl under stirring. The organic layer was concentrated and the residue washed throughly with light petroleum: the solid residue was identified as methylmercury chloride, while the solution afforded, on concentration, crude 3-cyano-5-phenylisoxazole (XVII), m.p. 75–85 °C. Precipitated with water from a DMSO solution: m.p.

86–91° (reported [7] m.p. 88–89 °C), identical (IR) with a sample prepared according to the literature [7]. IR (KBr): 2250w $cm^{-1}$. $^1H$ NMR ($CDCl_3$): 6.9s, 7.6–7.9m. $^{13}C$ NMR: 172.1s (C5), 140.1s (C3), 131.8d, 129.6d, 126.1d and 125.2s (Ph), 110.5 (C≡N), 103.3d (C4). *m/z*: 170 (100%, $M^+$), 140 (6, $M^+ - NO$), 105 (60, $PhCO^+$), 102 (4, $Ph-C{\equiv}CH^+$), 90 (12), 89(9), 77(40, $Ph^+$), 65 (metastable ion, 170 → 105).

*Reaction of Ib with methyl propiolate*

A solution of methylmercury fulminate (Ib, 1.82 g, 7.06 mmol) and methyl propiolate (0.63 ml, 7 mmol) in pure chloroform (90 ml) was refluxed for 3 h. The solvent was removed in vacuo and the residue treated with tetrachloromethane (130 ml). The solid obtained (0.77 g) was identified as starting material Ib and the residue of the $CCl_4$ solution was column-chromatographed (eluant: chloroform + light petroleum + THF, 20 : 1 : 0.5). The main fraction (yellow oil, 0.336 g, yield 16%) was distilled (oven 95 °C at 0.06 Torr) to give 0.233 g of colourless oil which solidified on cooling, m.p. 32–36 °C, identified as methyl methylmercurypropiolate. Found: C, 21.05; H, 2.03. $C_5H_6HgO_2$ calcd.: C, 20.10; H, 2.02%. IR (KBr): 2220, 1700 $cm^{-1}$. $^1H$ NMR: 0.3s 3.6s. $^{13}C$ NMR: 153.0s, 143.6s, 94.3s, 52.3q, 5.5q. $^{199}Hg$ NMR: −621q, $J(^{199}Hg-^1H)$ 164. *m/z*: 300 (8%, $M^+$), 269 (100, $M^+ - MeO$), 217 (16, $MeHg^+$), 202 (3, $Hg^+$), 97 (6), 67 (17), 59 (5), 55 (14), 39 (25, $MeC_2^+$).

## Acknowledgements

The following students have contributed to the Experimental: Lino Fabrizi, Andrea Perico and Cecilia Scarpi.

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