Participation by Adjacent Nitrogen during Solvolysis of Bridgehead Halide, 1-Chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane[1a]

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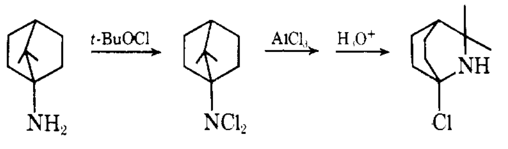
Abstract: The solvolysis of 1-chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane (**2**) was examined in 70% dioxane-water and in absolute ethanol. The sole products were 4-[2-amino-2-propyl]cyclohexanone (**8**) and 1-ethoxy-3,3-dimethyl-2-azabicyclo[2.2.2]octane (**9**), respectively. The first-order rate constants at 52° were (3.7 ± 0.13) $\times 10^{-4}$ and (2.6 ± 0.2) $\times 10^{-5}$ sec^{-1}, respectively. The corresponding carbon analogs, 1-bromo-3,3-dimethylbicyclo[2.2.2]octane (**6**) and 1-chloro-3,3-dimethylbicyclo[2.2.2]octane (**5**), have estimated rate constants of 1×10^{-7} and 2×10^{-9} sec^{-1}, respectively, at 52° in 70% dioxane-water. Chloride **2** reacts with silver ion more readily than either **5** or **6**. The increased stability of the bridgehead cation derived from **2** is ascribed to resonance interaction with the lone pair on adjacent nitrogen and favorable geometric effects. Reaction of **2** with ethanol was accelerated by base and presumably proceeds through a bridgehead imino intermediate which is converted to **9**. The hydrolytic stability of **9** is discussed. Comparisons are made with related heteroatom and carbocyclic systems.

The subject of bridgehead reactivity[2] has generated widespread interest in recent years. The solvolytic behavior of a considerable number of bridgehead halides in bicyclic and tricyclic systems has been examined. Recently, studies were reported (vide infra) on compounds in which a heteroatom (N, O, or S) is present in the ring system adjacent to the bridgehead position. The results of these investigations reflect the relative importance of inductive and resonance effects and also provide insight into the question of the limits of Bredt's rule.

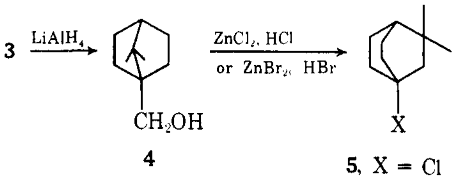
Our studies deal with the effect of neighboring nitrogen on the reactivity of bridgehead chloride in 1-chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane (**2**). This compound also provides the novel opportunity for base-promoted dehydrohalogenation to a bridgehead imino intermediate.

Synthetic Aspects. Compound **2** was obtained from rearrangement of 1-*N,N*-dichloroaminoapocamphane[1] (**1**) by exposure to aluminum chloride (eq 1). The parent amine was prepared as previously described except for a modification which resulted in an overall increase in yield: 10-camphorsulfonic acid → 10-camphorsulfonyl chloride[3] → 10-camphorchloro sulfoxide[3] → ketopinic acid[3,4] → 1-apocamphanecarboxylic acid[5] (**3**) → 1-aminoapocamphane.[5] Chlorination[1] of the amine was effected with *tert*-butyl hypochlorite.



1 **2** (1)

Both 1-chloro-3,3-dimethylbicyclo[2.2.2]octane (**5**) and 1-bromo-3,3-dimethylbicyclo[2.2.2]octane (**6**) were prepared from **3** according to the method of Sprecher.[6] The structure of **5** was confirmed by spectral comparison to **6** and by elemental analysis.



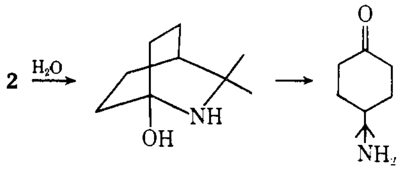
4

5, X = Cl
6, X = Br
7, X = OH

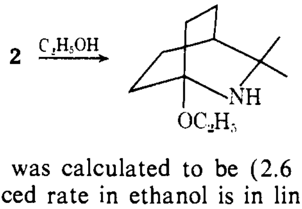
Solvolyses. Preliminary indication of the appreciable reactivity of **2** was obtained from its behavior during isolation from the reaction mixture. Mild conditions are required to prevent **2** from being hydrolyzed during conversion from the salt form to the free base in the presence of aqueous sodium hydroxide.

Chloride **2** reacted readily with aqueous silver nitrate at room temperature. In contrast, 4 hr was employed[7] to effect reaction with **6** under similar conditions. At 95–96° in 70% dioxane-water containing silver ion, **5** and **6** provided **7**, whereas no **7** was detected in the absence of silver ion under otherwise identical conditions. The yield of **7** from **5** corresponded well with the amount of silver chloride produced.

The solvolysis of **2** was examined quantitatively in aqueous dioxane and in ethanol. In 70% (by volume) dioxane-water, a single product was obtained, which was identified as 4-[2-amino-2-propyl]cyclohexanone[1] (**8**), eq 2. Kinetics were monitored by gas chromatographic determination of the concentrations of **2** and **8** in aliquots taken from the reaction mixture. First-order behavior to at least 90% completion was observed. In two runs at 52° and at concentrations of 0.065 and 0.098 *M*, rate constants of (3.7 ± 0.13) $\times$ 10^{-4} and (3.5 ± 0.3) $\times 10^{-4}$ sec^{-1} were obtained. In absolute ethanol, the sole product was ether **9**, identified by ir and NMR spectra and elemental analysis (eq 3). The rate constant at 52° was calculated to be (2.6 ± 0.2) $\times 10^{-5}$ sec^{-1}. The reduced rate in ethanol is in line with observations in other related cases, e.g., for *tert*-butyl bromide,[8] $k_{70\%\text{dioxane}}/k_{\text{ethanol}} = \sim 10^2$.



8 (2)



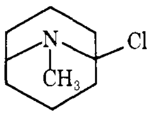
(3)

The solvolysis reaction was accelerated by base. With 2.5 *M* ethanolic sodium ethoxide, the half-life for disappearence of **2** was reduced from 450 to 5–10 min. Again, ether **9** was the sole product.

Discussion

Solvolytic Reactions. The prior literature[9] reveals that α-haloamines of the type $R_2CClNHR'$ prefer the ionic form $[R_2C{=}N^+HR']Cl^-$ in the open-chain series. On the other hand, incorporation of the α-haloamine structure into a bicyclic system results in a large decrease in lability of the bridgehead halide. The small number of known bicyclic, covalent α-chloroamines (or derivatives thereof)[10,11] are so constituted that the ionic form would contain a bridgehead trans double bond in a six-membered ring.

The solvolysis of **2** is clearly accelerated in comparison with the carbocyclic analog **6**. An estimated rate constant for **6** in 70% dioxane at 52° is 1×10^{-7} sec^{-1} (extrapolated from 100 and 131.2°).[7] With the usual difference[2d] in reactivity (factor of about 50) between chlorides and bromides, the rate constant for **5** at 52° is estimated to be $\sim 2 \times 10^{-9}$ sec^{-1}. Thus, the nitrogen adjacent to the bridgehead carbon produces a rate acceleration of nearly 2×10^5. This result compares nicely with a recent observation by Wiseman[11a] and coworkers who reported that 1-chloro-9-methyl-9-azabicyclo[3.3.1]nonane (**10**) solvolyzed nearly ten million times faster than its carbocyclic counterpart, 1-chlorobicyclo[3.3.1]nonane (**11**).



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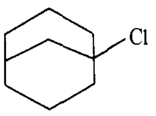
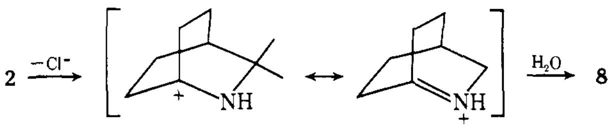


11

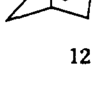
The nitrogen atom in **2** would be expected to destabilize the bridgehead cation **2a** on the basis of the inductive effect which has been estimated[10] in a somewhat different system to produce a rate decrease of 2×10^4 or 3×10^6. The increased lability of the chlorine in **2** under solvolytic conditions is, we believe, due to resonance stabilization of the bridgehead cation **2a** by the adjacent nitrogen. Thus, the total rate-enhancing resonance contribution of nitrogen in our system seems to be in the vicinity of 5×10^{10}. To invoke this type of argument in accounting for the reactivity of **2**, one must accept the immonium ion **2b** as a canonical resonance form which imparts a degree of carbon–nitrogen double bond character to the bridgehead position (Scheme I).

Scheme I



2a 2b

Wiseman[11a] drew similar conclusions to account for the greater reactivity of **10** over **11**. In related examples (**12**[11b] and **13**[12]) involving the oxygen heteroatom, it appears that resonance interaction must be important since a larger difference in the rates of reaction of **12** and **13** vs. their carbon analogs would be anticipated if the inductive effect were solely operative.



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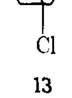
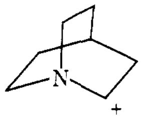


13

An examination of molecular models of **2** and **10** shows that the developing empty p orbital at the bridgehead bisects the angle formed by the orbitals comprising the lone pair and the NH or NCH_3 bond of adjacent nitrogen. Analogous geometry pertains for **12** and **13**.[12] The models further indicate that the angle between the nitrogen lone pair and the carbon–chlorine bond in **2** is about 60°. These orbitals will deviate even more toward perpendicularity as the hybridization changes toward sp^2. In addition, the geometric situation for overlap is made even less favorable because the orbitals on carbon and nitrogen are inclined away from each other. Apparently molecules like **2** and **10** can undergo some structural deformation by twisting and bending so that the geometric requirements for overlap are made more favorable.

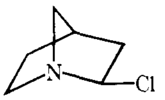
Several additional ideas appear reasonable.[13] If the CNC angle distorts more readily than one from CCC, then **2a**–**2b** can adjust to planarity easier than the ion from **6**. For a bridgehead cation in a carbocyclic system, sp^2 hybridization produces distortions in the molecule; in **2**, some of these distortions are already present due to the shorter C–N bond. Much of the unreactivity of **6** is a consequence of bridgehead–bridgehead repulsion[2b] as the carbonium ion attempts to attain planarity; in **2**, the shorter C–N bond brings the bridgeheads closer together in the ion precursor, thereby reducing the strain increase on ionization, i.e., **2** is already partially up the energy hill which must be climbed during ionization.

A related example in the bicyclo[2.2.2]octyl system was disclosed by Grob and Sieber[14] in which the positions of nitrogen and electron deficient carbon were reversed. On the basis of the observation that the 2-quinuclidinyl cation **14** is somewhat more stable than its carbon analog, they proposed delocalization involving the bridgehead nitrogen.



14

The work of Gassman[10] and coworkers is also noteworthy. They found that methanolysis of **15** proceeded at roughly the same rate as **16**. Although the geometric configuration for orbital overlap in **17** might on superficial examination appear to be similar to that in **2a**, the greater reluctance of **18** to participate to a significant extent in the stabilization of **17** reflects the greater degree of strain inherent in **18** as opposed to **2a** and **14**. This is in harmony with Wiseman's[15] generalization that the strain of a bridgehead double bond is closely related to the strain of the corresponding *trans*-cycloalkene. Similarly, olefin **19**[16a] is generated readily under Hofmann elimination conditions, whereas olefin **20**[16b] is formed to only a very minor extent.



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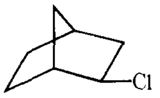

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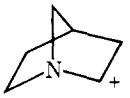

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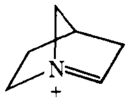

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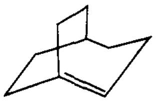

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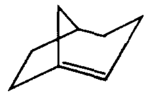

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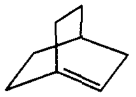
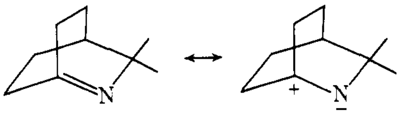
The related carbon analog of **2b**, bicyclo[2.2.2]oct-1-ene (**21**),[17] is purportedly generated as a transient species in the



21

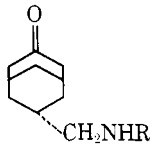
reaction of 2-bromo-1-ethoxybicyclo[2.2.2]octane with *tert*-butyllithium.

Base-Promoted Elimination. The reaction of **2** under basic conditions may fall into the category of E2 elimination. Accordingly, compound **2** might undergo concerted dehydrochlorination leading to the strained bridgehead imine **22a** (ylid **22b** as a possible contributor[13]) which

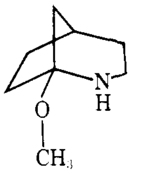


22a **22b**

would be readily attacked by ethoxide ion, possibly assisted by solvent coordination on nitrogen. Alternatively, a two-step process, E1cB mechanism, may be operative. Abstraction of the proton from nitrogen and subsequent loss of chloride ion generates **22**, the precursor of **9**. Related bridgehead imino structures have been postulated in the reduction of **23a** to 4-azahomoadamantane[18,19] and of **24** to



23a, R = H
23b, R = C_2H_5

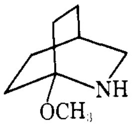


24

2-azabicyclo[3.2.1]octane[20] by lithium aluminum hydride. Evidence has also been presented for analogous type unsaturation in the 2-azabicyclo[3.3.1]non-1-ene system.[21,22]

The most favored geometry for β elimination generally consists of the leaving groups arranged in an anti or trans coplanar arrangement. However, a substantial number of examples are known in which a cis elimination (syn conformation) route is followed.[23,24] In certain rigid bicyclic systems, e.g., 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracenes, syn dehydrochlorination predominates over the anti pathway.[25] It is apparent that elimination can occur, albeit less favorably, in systems whose geometry deviates from coplanarity, as in **10, 13,** and other cases.[25]

Hydrolytic Stability of α-Amino Ethers. In agreement with previous observations[20,26] on related materials, compound **9** was stable under acidic conditions. In the case of open chain types, α-amino ethers hydrolyze readily in acid through an iminium ion $R_2N^+{=}CH_2$.[27] Reed and Lwowski[20] were able to effect hydrolysis of **24** and **25** by prolonged heating with acid. In the tricyclic series, on acid hydrolysis, **26** readily underwent ring cleavage[18,19] to **23**, eq 4.



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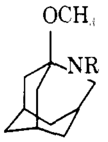

$\longrightarrow$ **23a** or **23b** (4)

26, R = H or C_2H_5

If an iminium ion is involved, then the mechanistic discussion in the solvolysis section would pertain here.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer 137 instrument, calibrated with the 1601 cm^{-1} band of polystyrene. A Varian T-60 instrument was used to obtain NMR data which are reported in parts per million relative to tetramethylsilane as internal standard. Gas chromatography was carried out with a Varian instrument (Model 1700) with a 10 ft × 0.25 in. column of 20% Carbowax 20M on Chromosorb P (30-60) (column A) or a 10 ft × 0.25 in. column of UCON50HB2000 and 5% NaOH on Chromsorb W (45-60) (column B).

Solutions were dried over Na_2SO_4. 10-Camphorsulfonic acid and dioxane (gold label spectrophotometric grade) were obtained from the Aldrich Chemical Co. and used without further purification. Microanalyses were performed by the Baron Consulting Co., Orange, Conn. Dioxane (70%) was prepared by pipetting 140 ml of dioxane into a 200-ml volumetric flask and diluting to the mark with doubly distilled water.

1-Chloro-3,3-dimethyl-2-azabicyclo[2.2.2]octane (2) was prepared as described previously.[1] Chlorination of **1** with *tert*-butyl hypochlorite was effected in low boiling petroleum ether, instead of in cyclopentane, with no decrease in yield. The product was isolated by preparative GLC (column B) and further purified by sublimation at reduced pressure. Typically, 5.0 g of 1-aminoapocamphane hydrochloride yielded 50-60 mg (1%) of pure **2**, mp 56-57° (lit.[1] mp 55-56°).

1-Hydroxymethylapocamphane (4). Acid **3** (3 g, 18 mmol) was reduced with 2.5 g of $LiAlH_4$ in 150 ml of dry ether. Work-up yielded 2.5 g (90%) of crude **4**. A pure sample was obtained via preparative GLC (column A) and sublimation: mp (sealed tube) 198-200° (lit.[6] mp 199-200°); NMR ($CDCl_3$) δ 0.93 (s, 6, CH_3) and 3.63 (s, 2, CH_2O).

1-Chloro-3,3-dimethylbicyclo[2.2.2]octane (5). The crude alcohol **4** (1.88 g) was treated with zinc chloride (15 g) and concentrated hydrochloric acid (25 ml). After the initial bubbling had subsided, the reaction mixture was stirred overnight at room temperature, followed by heating at 90-95° for 4 hr. After cooling and addition of 50 ml of water, the product was extracted with pentane. The combined extract was washed with 10% sodium carbonate, water, and dried. Solvent removal afforded crude **5** (1.7 g, 80%). Pure samples of **5** were obtained by preparative GLC (column A): bp (micro) 210-212°; ir (neat) 1372 and 1351 cm^{-1} (*gem*-dimethyl); NMR ($CDCl_3$) δ 1.05 (s, 6 H, CH_3, overlapping a multiplet of 1 H) and 1.75-2.67 (complex multiplet, 10 H, CH_2); mass spectrum *m/e* (rel intensity) 172 (5) (M^+), 157 (100), 121 (53), 93 (44), and 81 (44).

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.55; H, 9.93; Cl, 20.53. Found: C, 69.30; H, 9.95; Cl, 20.91.

1-Bromo-3,3-dimethylbicyclo[2.2.2]octane (6). The procedure of Sprecher[6] was followed, similar to that for **5**, with **4** (1 g), zinc bromide (10 g), and 48% HBr (20 ml). After work-up, there was obtained 1.15 g (90%) of crude **6**. Preparative GLC (column A) and sublimation produced a pure sample: mp 59.5-61.5° (lit.[6] mp 62-62.5°); ir (CCl_4) 1390 and 1370 cm^{-1} (*gem*-dimethyl); NMR ($CDCl_3$) δ 1.05 (s, 6, CH_3, overlapping a complex multiplet of 1 H) and 2.2 (multiplet, 10 H, CH_2).

2 and Dioxane-Water. A 45-mg sample of **2** was placed in a stoppered flask kept in a water bath thermostated at 52.1 ± 0.1°. Preheated, 70% dioxane (4.0 ml) was quickly added, and the reaction was allowed to proceed with agitation provided by means of a water-driven stirrer. Aliquots were removed periodically, treated with a small amount of solid anhydrous potassium carbonate, followed by quick cooling with Dry Ice-acetone. The aliquots were analyzed as soon as possible by GLC (column B). The percentages of **2** and **8** were determined using known compositions of **2** and **8**. The reaction was allowed to proceed for at least 1.5-2 hr. The data were plotted, resulting in good straight lines. Slopes were obtained by least-squares treatment of the data. The rate constant from the above procedure was found to be 3.70×10^{-4} sec^{-1}.

The above process was repeated with 34 mg of **2** and 2.0 ml of 70% dioxane. The rate constant was determined to be 3.45×10^{-4} sec^{-1}.

2 and Absolute Ethanol. A 42-mg sample of pure **2** in 1.0 ml of absolute ethanol was thermostated at 52.1 ± 0.1° with agitation. Aliquots were removed periodically and treated with solid anhydrous potassium carbonate after quenching by means of cooling with an ice-salt mixture. GLC analysis (column B) was performed immediately, and the percentages of **2** and **9** were determined by comparison with known mixtures of **2** and **9**. After 2.0 hr, 69% of **2** remained unreacted. The appropriate data were plotted, and the slope was determined by the least-squares method. The rate constant was found to be 2.58×10^{-5} sec^{-1}.

After the reaction mixture was heated at reflux overnight, a sample of **9** was isolated by preparative GLC (isolated yield, 55-60%): ir (CCl_4) 2950, 1380, 1365, 1120, 1090, 1045, and 1020 cm^{-1}; NMR (CCl_4) δ 1.03 (t, 3, CH_2CH_3), 1.13 (s, 6, CH_3), 3.50 (q, 2, CH_2CH_3).

Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 72.38; H, 11.30; N, 7.84.

2 and Ethanolic Sodium Ethoxide. Clean metallic sodium (565 mg, 0.0246 g-atom) was reacted with 10.0 ml of absolute ethanol with cooling. A portion (2.0 ml) of the solution was added to **2** (38 mg, 0.22 mmol) in a stoppered flask, and the solution was thermostated at 52.0 ± 0.1° with agitation. After 15 min, GLC analysis of a small aliquot showed 10% of **2** and 90% of **9**. After 40 min, a second aliquot contained 5% of **2** and 95% of **9**. The reaction mixture was quenched with water (2 ml) and made acid to litmus with 18% HCl. The volatile solvents were removed under reduced pressure, and the resulting solution was made basic with 50% NaOH. The solution was extracted with pentane which was concentrated by evaporation. The product was isolated by preparative GLC (isolated yield, 55%). The NMR spectrum was identical with that for the sample obtained from the reaction of **2** with ethanol.

5 and 70% Dioxane. A sealed tube containing **5** (112 mg, 0.65 mmol) and 0.50 ml of 70% dioxane was heated at 95-96° with agitation for 3.5 hr by complete immersion in an oil bath. The reaction was quenched by freezing with Dry Ice-acetone. After the tube was opened, the contents were taken up in 1-2 ml of methylene chloride and dried. GLC analysis (column A) showed the presence of only unreacted **5** and none of the alcohol product **7**.

5 and Silver Ion. The procedure for **5** in 70% dioxane was carried out with **5** (95 mg, 0.55 mmol) and silver nitrate (218 mg, 1.28 mmol). Work-up and analysis via GLC indicated the presence of **5** (65%) and **7** (35%). A sample of **7** was collected, mp 111-113° (lit.[6] mp 115.5-116.5°). The NMR spectral similarity to **5** and **6** provides additional support for the structure of **7**. When the same reaction was conducted with an altered molar ratio, **5** (145 mg, 0.84 mmol) and silver nitrate (191 mg, 1.12 mmol), 81% of **5** was unchanged, with 19% converted to **7**.

6 and 70% Dioxane. The procedure for **5** was followed using **6** (53 mg, 0.24 mmol). GLC analysis (column A) after work-up pointed to the presence of unreacted **6** only.

6 and Silver Ion. When the same conditions were used with **6** (96 mg, 0.44 mmol) and silver nitrate (144 mg, 0.85 mmol), there resulted 21% of unreacted **6** and 79% of **7**, identified by GLC retention time.

5 and Silver Ion. A mixture of **5** (235 mg, 1.36 mmol), silver nitrate (108 mg, 0.63 mmol), and 2.0 ml of 70% dioxane-water in a sealed tube was heated for 5 hr at 96 ± 1° by means of an oil bath. The tube was cooled and opened, and the AgCl was removed by filtration. The solid was washed with a small volume of methylene chloride which was combined with the filtrate. The AgCl was further washed with acetone and air dried to constant weight (80 mg) in the dark. This corresponds to 41% reaction of **5**. The filtrate was dried (Na_2SO_4) and examined by GLC (column A). Comparison of the results with known mixtures of **5** and **7** showed that 40% of **5** had reacted.

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References and Notes

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