Hydroperoxynaphthalenones from the Mild Autoxidation of Certain Simple 1-Alkyl-2-naphthols

By **John Carnduff** * and **David G. Leppard**, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland †

1-Isopropyl- and 1-cyclohexyl-2-naphthol react with oxygen in benzene at room temperature and in the absence of catalysts or bases to give 1-alkyl-1-hydroperoxynaphthalen-2(1*H*)-ones in high yield as the sole products. 1-Ethyl-2-naphthol, however, yields a mixture of the analogous hydroperoxide plus the product of O–C coupling of the phenoxyl radical. 1-Benzyl- and 1-methyl-2-naphthol do not react with oxygen under these conditions.

THERE is a relatively small group of organic substances which react with oxygen at room temperature in the absence of catalysts or bases and which give a single product in good yield, and an even smaller group, including certain hydrocarbons,[1] enamines,[2] enols,[3] and phenols,[4] mild autoxidation of which involves uptake of 1 mol. equiv. of oxygen to give a hydroperoxide. Our chance observation that 1-isopropyl-2-naphthol (1d) belongs in this latter group, whereas 1-methyl-2-naphthol does not, led us to study the autoxidation of a range of 1-alkyl-2-naphthols. We report here the behaviour of the methyl, ethyl, benzyl, isopropyl, and cyclohexyl cases.[5]

Fries [6] reported that solid 1-methyl-2-naphthol was partly converted after several years into the hydroxynaphthalenone (3a), and that traces of (3a) were detectable after oxygen had been bubbled into a solution of the naphthol in benzene for 4 weeks. No hydroperoxide was observed. He also noted [7] that 1-ethyl-2-naphthol was unstable in air, the white crystals becoming grey and oily. 1-Benzyl-[8] and some higher 1-n-alkyl-2-naphthols [9] have occasionally been reported but there is no comment on their stability in air.

1-Cyclohexyl-2-naphthol was reported [10] to react with air to give yellow crystals of a 1 : 1 adduct showing characteristic reactions of a peroxide or hydroperoxide but no structure was allocated to it. 1-Isopropyl-2-naphthol has been reported twice [11,12] with no comment on its stability in air, and 1-t-butyl-2-naphthol was unknown until recently, when its rapid autoxidation was reported.[13]

The preparation of the series of 1-alkyl-2-naphthols has required a variety of synthetic approaches. We have found the most convenient synthesis of 1-methyl-2-naphthol to be the direct reduction of 1-formyl-2-naphthol with sodium dihydro(bis-2-methoxyethoxy)-aluminate in refluxing xylene.[14] 1-Ethyl-2-naphthol is easily prepared by the analogous reduction of 1-acetyl-2-naphthol, which can be made by the direct acetylation of 2-naphthol with the acetic acid–boron trifluoride complex [15]—a procedure which in our hands is more effective than the classical Fries rearrangement of 2-naphthyl acetate.

1-Isopropyl-2-naphthol has been made by alkylation of 2-naphthol with propan-2-ol and a zinc chloride catalyst,[12] by reductive cleavage of 1-methylnaphtho-[2,1-*b*]furan,[11] and from 1-acetyl-2-naphthol by reaction with methylmagnesium bromide and hydrogenation of the isopropenylnaphthol.[11] We sought a direct synthesis in the alkylation of solid sodium 2-naphthoxide suspended in boiling toluene with isopropyl halides—a technique known [8,16] to give good percentages of *C*-alkylation especially with reactive, *e.g.* benzylic, halides. In an attempt to maximise the yield, various metal naphthoxides and various isopropyl halides were tried.[17] Of the cations Li^+, Na^+, K^+, and IMg^+ only Na^+ gave good yields. Isopropyl iodide gave mainly *O*-alkylation. Highest yields were obtained by using *ca.* 1.3 mole of sodium naphthoxide per litre of toluene and batchwise addition of an excess of isopropyl bromide over about 24 h to the refluxing suspension. Distillation of the products under reduced pressure allowed removal of 2-naphthol and any ether. The higher boiling fractions yielded over 70% of 1-isopropyl-2-naphthol, which could be further purified by crystallisation under nitrogen. A similar procedure was used to make 1-benzyl- and 1-cyclohexyl-2-naphthols.

The naphthols were each autoxidised by shaking approximately 0.2M-solutions in benzene with oxygen at 1 atm in daylight. In the case of 1-isopropyl-2-naphthol, deposition of yellow crystals began after several hours and after about 20 h uptake ceased at

† Part of this work was carried out at the University of Dundee, Scotland

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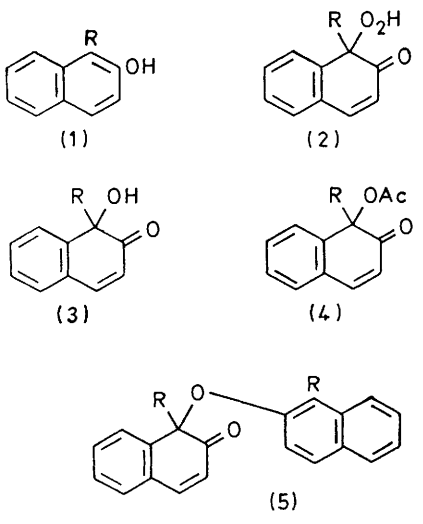
close to the theoretical volume for 1 : 1 reaction. The benzene solution yielded the 1 : 1 adduct in about 80% yield and no other product or starting material was detected by t.l.c. of the mother liquors. The spectra of the product reveal a typical naphthalen-2(1*H*)-one chromophore, a hydrogen-bonded hydroxy-group and a hydrogen-bonded carbonyl group. In the n.m.r. spectrum, the isopropyl methyl signals are found at slightly different fields owing to the adjacent chiral centre, the hydroxy-signal is at low field (τ 0.43) owing to hydrogen bonding, and the β-proton signal of the enone system appears among the benzene ring proton signals. The presence of a hydroperoxy-group is confirmed by the immediate oxidation of iodide or iron(II) and the compound could be reduced quantitatively to a hydroxynaphthalenone (3d) by iodide ion, dimethyl sulphide, or catalytic hydrogenolysis.

Autoxidation of 1-cyclohexyl-2-naphthol under the same conditions yielded, after a slightly longer time, a high yield of a yellow solid with the properties described



a; R = Me
b; R = Et
c; R = CH_2Ph
d; R = Pr^i
e; R = cyclohexyl

by Alberti.[10] Again no other products were detected. The spectra and chemical reactions of this product are similar to those of the isopropyl case, and it must be assigned the structure (2e). Reduction with hydrogen or iodide gave (3e). Autoxidation of 1-ethyl-2-naphthol under the same conditions was slower. Uptake ceased after 73 h when about half of the volume calculated for a 1 : 1 adduct had been absorbed. Fractional crystallisation of the products yielded two materials. The first to crystallise was the product (5b) of C–O coupling of the naphthoxyl radical, identified from its spectra and its independent synthesis by oxidation of 1-ethyl-2-naphthol with hexacyanoferrate(III). The second autoxidation product was the hydroperoxide (2b), identified by its spectra and its reduction by iodide ion. The mother liquors from crystallisation of the autoxidation products still contained a little 1-ethyl-2-naphthol. The autoxidation of 1-ethyl-2-naphthol appears therefore to be slower than that of the secondary alkyl-2-naphthols and does not lead exclusively to uptake of oxygen by the phenol. Autoxidation of 1-benzyl-2-naphthol was tried under the same conditions. After 5 days virtually no oxygen had been absorbed and t.l.c. revealed no products. Autoxidation of 1-methyl-2-naphthol under the same conditions also failed. After 8 days virtually no oxygen had been absorbed and t.l.c. of the benzene solution revealed the presence only of the starting phenol.

The autoxidation of the isopropylnaphthol was repeated in the presence of 2,6-di-t-butyl-*p*-cresol. This delayed significant absorption of oxygen for 90 min. Uptake then proceeded as in the uninhibited case and the only product derived from the isopropylnaphthol was the hydroperoxide (2d). When the autoxidation was repeated in the presence of 7 mole % of cobalt(III) acetylacetonate, theoretical uptake of oxygen was complete in only 3 h and the hydroperoxide was again the only detected product. These results support the supposition of a normal radical chain autoxidation for which the initiation process(es) can be accelerated by the cobalt(III). Cobalt(III) acetylacetonate however did not induce autoxidation of 1-methyl-2-naphthol. When it was added to the autoxidation system there was no oxygen uptake and t.l.c. revealed only unchanged starting phenol.

Since the phenoxyl radical dimers (5) were possible autoxidation products they were prepared from the methyl-, ethyl-, and isopropyl-naphthols by oxidation with hexacyanoferrate(III). In each case the O–C(1) coupled dimer was the only one found.[18] The structures are supported by the u.v. spectra, which are superpositions of naphthalenone and 2-naphthyloxy absorptions. The n.m.r. spectra in each case show one aryl proton signal as a doublet at high field (τ *ca.* 4.0). This is presumably due to H-3 of the naphthalene, which must be shielded because the molecule adopts a folded conformation in which this proton lies above the plane of the naphthalenone. A less marked shielding (τ 3.13) has been observed for one proton in the analogous ' dimer ' from 1-methoxy-2-naphthol.[19] The dimer (5b) was formed in the autoxidation of 1-ethyl-2-naphthol but neither of the other dimers was formed during oxygenation of the parent naphthols. As a chemical confirmation of the structures of the hydroperoxides the hydroxyisopropylnaphthalenone (3d), made by reduction of the hydroperoxide, was independently synthesised by

[18] The methyl compound is well known: L. I. Smith and J. W. Horner, *J. Amer. Chem. Soc.*, 1938, **60**, 676; R. Pummerer and I. Viet, *Chem. Ber.*, 1953, **86**, 412.

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Wessely acetoxylation of 1-isopropyl-2-naphthol with lead tetra-acetate [20] to give (4d) and mild basic hydrolysis of the acetate group.

We conclude that simple 1-alkyl-2-naphthols react cleanly and fairly rapidly with oxygen to give hydroperoxynaphthalenones if the alkyl group is secondary but not if it is primary.

EXPERIMENTAL

M.p.s were taken with a Kofler hot-stage apparatus. Unless otherwise stated u.v. spectra were measured for solutions in ethanol and i.r. spectra for Nujol mulls. N.m.r. spectra were run in deuteriochloroform with tetramethylsilane as internal standard. Light petroleum refers to the fraction b.p. 60—80 °C. T.l.c. was carried out on Kieselgel G with 20% ethyl acetate in light petroleum unless otherwise stated. 1-Methyl-2-naphthol was prepared by reduction of commercial 1-formyl-2-naphthol with sodium dihydrobis-(2-methoxyethoxy)aluminate.[14] 1-Acetyl-2-naphthol was prepared by acetylation of 2-naphthol with acetic acid–boron trifluoride complex [15] and reduced to 1-ethyl-2-naphthol with sodium dihydrobis-(2-methoxyethoxy)aluminate.

1-*Isopropyl*-2-*naphthol* (1d).—AnalaR 2-naphthol (15.0 g) was added to a solution of sodium (2.4 g) in dry methanol. The methanol was evaporated off and replaced by dry toluene, and then the toluene was evaporated off. Addition and removal of toluene was repeated twice. The dry sodium naphthoxide was powdered and suspended in dry toluene (75 ml). The suspension was heated to 120 °C under reflux and under nitrogen and vigorously stirred. 2-Bromopropane (total 40 ml) was added in batches over 24 h while stirring and reflux continued. After cooling, water was added, the water layer was washed with toluene, and the combined toluene layers were washed with water, dried, and evaporated to yield a red oil which was distilled under vacuum. The fraction b.p. 98—104° at 0.01 mmHg was 1-isopropyl-2-naphthol (14.6 g, 74%). Recrystallisation from benzene gave needles, m.p. 72—74° (lit.,[11] 72—74°); $\nu_{max.}$ 3 200, 810, and 745 cm^{-1}; $\lambda_{max.}$ 232, 271, 280.5 292, 325, and 337 nm (ε 60 300, 3 980, 4 890, 4 070, 2 400, and 2 570), τ (CCl_4) 8.55 (6 H, d, *J* 7 Hz), 6.17 (1 H, sept, *J* 7 Hz), 5.25 (1 H, s, exchangeable with D_2O), and 1.9—3.5 (6 H, m).

1-*Cyclohexyl*-2-*naphthol* (1e).—Powdered sodium 2-naphthoxide was prepared as above from 2-naphthol (10.0 g) and suspended in dry toluene (40 ml). Bromocyclohexane (26 g) was added and the mixture refluxed under nitrogen for 24 h. After cooling, water was added and the toluene layer separated, dried, and evaporated to give a red oil, which was distilled under reduced pressure. The fraction with b.p. 172—180° at 2 mmHg consisted of 1-cyclohexyl-2-naphthol (5.4 g). Crystallisation from methylcyclohexane gave white plates, m.p. 106—108° (lit.,[10] 107—108°).

1-*Benzyl*-2-*naphthol* (1c).—Sodium 2-naphthoxide was prepared from 2-naphthol (20 g) as above and suspended in refluxing toluene under nitrogen. Benzyl bromide (27.0 g) was added and reflux continued for 7 h. After cooling, water was added and the toluene layer extracted with Claisen's alkali. Acidification of this alkaline extract yielded an oil which was distilled under reduced pressure. The fraction with b.p. 120—155° at 0.01 mmHg consisted of 1-benzyl-2-naphthol (20 g). Crystallisation from benzene gave white needles, m.p. 110—111.5° (lit.,[8] 110—111°).

Autoxidation of 1-*Isopropyl*-2-*naphthol*.—Freshly recrystallised 1-isopropyl-2-naphthol (0.93 g) was dissolved in benzene (25 ml) and shaken with oxygen at 1 atm in diffuse daylight. After about 3 h pale yellow crystals of the hydroperoxide began to precipitate. After 22 h, 101 ml of oxygen had been absorbed (theory 112 ml) and uptake ceased. The benzene solution was concentrated and the product allowed to crystallise out, yielding 1-*hydroperoxy*-1-*isopropylnaphthalen*-2(1H)-*one* (0.7 g, 75%) as yellow rhombs, m.p. 135—137°; $\nu_{max.}$ 3 300 and 1 660 cm^{-1}; $\lambda_{max.}$ 234, 240, and 313 nm (ε 14 790, 15 490, and 8 320); τ 9.18 (3 H, d, *J* 7 Hz), 9.15 (3 H, d, *J* 7 Hz), 7.87 (1 H, sept, *J* 7 Hz), 3.86 (1 H, d, *J* 10 Hz), 2.3—2.8 (5 H, m), and 0.43 (1 H, exchangeable with D_2O) (Found: C, 71.3; H, 6.3. $C_{13}H_{14}O_3$ requires C, 71.55; H, 6.45%). T.l.c. of the mother liquors indicated the presence of further hydroperoxide and the absence of any other product.

Autoxidation of 1-*Cyclohexyl*-2-*naphthol*.—Freshly crystallised 1-cyclohexyl-2-naphthol (1.13 g) was dissolved in benzene (25 ml) and shaken with oxygen in the manner described above. After 4 days uptake ceased. T.l.c. showed the presence of one species only in the solution. The benzene solution was concentrated and on cooling deposited yellow crystals of 1-*cyclohexyl*-1-*hydroperoxynaphthalen*-2(1H)-*one* (2e) (1.0 g, 77%), m.p. 179—181°; $\nu_{max.}$ 3 200, 1 660, and 770 cm^{-1}; $\lambda_{max.}$ 236, 241, and 316 (ε 13 180, 13 800, and 7 760); τ 8.0—9.2 (11 H, m), 3.92 (1 H, d, *J* 10 Hz), 2.3—2.8 (5 H, m), and 1.17 (1 H, exchangeable with D_2O) (Found: C, 74.2; H, 7.0. $C_{16}H_{18}O_3$ requires C, 74.4; H, 7.0%).

Autoxidation of 1-*Ethyl*-2-*naphthol*.—Freshly crystallised 1-ethyl-2-naphthol (0.83 g) was dissolved in benzene (25 ml) and shaken with oxygen as above. After 73 h uptake had amounted to 52 ml (calculated for 1 : 1 reaction, 108 ml) and had ceased. The benzene was evaporated off and ethanol added to the oily residue. Crystals formed slowly. Recrystallisation of these from ethanol gave the 'dimer' (5b) (0.46 g). Concentration of the original mother liquors led to deposition of a different material. Recrystallisation of this from ethanol gave rhombs of 1-*ethyl*-1-*hydroperoxynaphthalen*-2(1H)-*one* (2b) (0.25 g), m.p. 115—116°; $\nu_{max.}$ 3 300, 1 665, and 765 cm^{-1}; $\lambda_{max.}$ 233, 239, and 314.5 (ε 13 490, 13 800, and 7 940); τ 9.3 (3 H, t, *J* 7 Hz), 8.16 (2 H, q, *J* 7 Hz), 3.88 (1 H, d, *J* 10 Hz), 2.2—2.9 (5 H, m), and 0.3 (1 H, exchangeable with D_2O) (Found: C, 70.7; H, 6.0. $C_{12}H_{12}O_3$ requires C, 70.55; H, 5.9%).

1-*Hydroxy*-1-*isopropylnaphthalen*-2(1H)-*one* (3d).—1-Hydroperoxy-1-isopropylnaphthalen-2(1*H*)-one (3.0 g) was dissolved in ethanol (50 ml) and treated with potassium iodide (0.5 g) in water (10 ml). The liberated iodine was destroyed by adding aqueous sodium thiosulphate and then more water was added (200 ml) and the mixture extracted with ether. The ether layer was washed with water, dried, and evaporated to yield 1-*hydroxy*-1-*isopropylnaphthalen*-2(1H)-*one* (2.70 g, 98%), which crystallised from ethanol as pale yellow rhombs, m.p. 88—89°; $\nu_{max.}$ 3 400, 1 660, and 760 cm^{-1}; $\lambda_{max.}$ 236.5 and 312.5 nm (ε 12 300 and 6 600); τ 9.18 (3 H, d, *J* 7 Hz), 9.15 (3 H, d, *J* 7 Hz), 7.95 (1 H, sept, *J* 7 Hz), 6.2 (1 H, exchangeable with D_2O), 3.86

[20] F. Wessely, G. Lauterbach-Keil, and F. Sinwell, *Monatsh.*, 1950, **81**, 811.

(1 H, d, *J* 10 Hz), and 2.3—2.8 (5 H, m) (Found: C, 77.25; H, 7.05. $C_{13}H_{14}O_2$ requires C, 77.2; H, 6.95%).

1-*Cyclohexyl*-1-*hydroxynaphthalen*-2(1H)-*one* (3e).—1-Cyclohexyl-1-hydroperoxynaphthalen-2(1*H*)-one (0.5 g) was reduced by addition of potassium iodide and then thiosulphate ion as above to yield 1-*cyclohexyl*-1-*hydroxynaphthalen*-2(1H)-*one* (0.43 g, 93%), which crystallised from aqueous ethanol as golden needles, m.p. 91—92°; $\nu_{max.}$ 3 400, 1 660, and 760 cm^{-1}; $\lambda_{max.}$ 235 and 312.5 nm (ε 19 500 and 5 620); τ 8.0—9.2 (11 H, m), 6.18 (1 H, exchangeable with D_2O), 3.87 (1 H, d, *J* 10 Hz), and 2.2—2.8 (5 H, m) (Found: C, 79.2; H, 7.45. $C_{16}H_{18}O_2$ requires C, 79.35; H, 7.45%).

1-*Isopropyl*-1-(1-*isopropyl*-2-*naphthyloxy*)*naphthalen*-2(1H)-*one* (5d).—1-Isopropyl-2-naphthol (2.0 g) in ether (100 ml) was mixed with a solution of potassium hexacyanoferrate(III) (10.0 g) and sodium hydroxide (2.2 g) in water (100 ml). The two-phase mixture was stirred at room temperature for 2 h. The ether layer was washed with water, dried, and evaporated and the residue chromatographed on silica. Elution with 5% ether in light petroleum and crystallisation of the eluted material from ethanol gave the '*dimer*' as yellow crystals (1.0 g), m.p. 141—143°; $\nu_{max.}$ 1 665, 805, and 745 cm^{-1}; $\lambda_{max.}$ 234, 283, 294, and 316 nm (ε 82 100, 9 100, 10 300, and 9 950); τ 9.05 (6 H, d, *J* 7 Hz), 8.38 (6 H, d, *J* 7 Hz), 7.66 (1 H, sept), 5.90 (1 H, sept), 4.20 (1 H, d, *J* 9 Hz), 3.95 (1 H, d, *J* 10 Hz), and 1.9—3.2 (10 H, m) (Found: C, 84.1; H, 6.8. $C_{26}H_{26}O_2$ requires C, 84.3; H, 7.05%).

1-*Ethyl*-1-(1-*ethyl*-2-*naphthyloxy*)*naphthalen*-2(1H)-*one* (5b).—1-Ethyl-2-naphthol was oxidised as above. Evaporation of the ether layer and crystallisation from ethanol gave the '*dimer*' as a yellow solid, m.p. 145—147°; $\nu_{max.}$ 1 660, 810, and 750 cm^{-1}; $\lambda_{max.}$ 232, 282.5, 294, and 312.5 nm (ε 85 100, 9 330, 10 960, and 10 230); τ 9.0 (3 H, t, *J* 7 Hz), 8.58 (3 H, t, *J* 7 Hz), 7.85 (2 H, q, *J* 7 Hz), 6.70 (2 H, q, *J* 7 Hz), 4.01 (1 H, d, *J* 8.5 Hz), 3.71 (1 H, d, *J* 10 Hz), and 1.9—3.0 (10 H, m) (Found: C, 83.95; H, 6.45. $C_{24}H_{22}O_2$ requires C, 84.2; H, 6.45%).

1-*Methyl*-1-(1-*methyl*-2-*naphthyloxy*)*napthalen*-2(1H)-*one* (5a).—1-Methyl-2-naphthol (4.5 g), sodium hydroxide (12 ml; 15%), saturated brine (60 ml), and water (220 ml), were stirred together in an ice-bath and potassium hexacyanoferrate(III) (9.7 g) in water (57 ml) added slowly. After a further 2 h, the precipitate was filtered off, washed with water, and dried. The solid was recrystallised from aqueous acetone and then from ethanol giving the '*dimer*' as yellow microcrystals (2.7 g, 60%), m.p. 132—134° (lit.,[18] 131—132.5°); $\nu_{max.}$ 1 690 cm^{-1}; $\lambda_{max.}$ 232, 282.5, 293.5, and 312 nm (ε 77 620, 8 710, 10 470, and 9 770); τ 8.19 (3 H, s), 7.24 (3 H, s), 3.97 (1 H, d, *J* 9 Hz), 3.66 (1 H, d, *J* 10 Hz), and 1.95—2.90 (10 H, m).

1-*Acetoxy*-1-*isopropylnaphthalen*-2(1H)-*one* (4d).—1-Isopropyl-2-naphthol (1.0 g) in glacial acetic acid (30 ml) was treated with freshly crystallised lead tetra-acetate (2.6 g) and the slurry set aside with occasional shaking for 24 h. Most of the acetic acid was removed under vacuum and water added. The mixture was extracted with ether (4 × 100 ml) and the combined ether layers were washed with aqueous sodium hydrogen carbonate, dried, and evaporated to give 1-*acetoxy*-1-*isopropylnaphthalen*-2(1H)-*one* (1.1 g, 84%), which crystallised from ethanol as needles, m.p. 77°; $\nu_{max.}$ 1 730 and 1 675 cm^{-1}; $\lambda_{max.}$ 233, 238, and 309 nm (ε 12 880, 13 800, and 8 500); τ 9.20 (3 H, d, *J* 7 Hz), 9.15 (3 H, d, *J* 7 Hz), 8.00 (3 H, s), 7.95 (1 H, sept, *J* 7 Hz), 3.98 (1 H, d, *J* 10 Hz), 2.78 (1 H, d, *J* 10 Hz), and 2.8 (4 H, narrow m) (Found: C, 73.5; H, 6.6. $C_{15}H_{18}O_3$ requires C, 73.75; H, 6.55%).

Hydrolysis of the Acetate (4d).—The acetate (4d) (0.2 g) was dissolved in water (25 ml), ethanol (20 ml), and sodium hydroxide (7 ml; 1M). After 4 h at room temperature, the mixture was poured into water and extracted with ether. The ether layers yielded 1-hydroxy-1-isopropylnaphthalen-2(1*H*)-one (0.13 g, 78%), m.p. 86—89°, identical with the material obtained by reduction of the hydroperoxide.

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