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Photochemical hydrogen abstraction by benzophenones from hydrogen donors in the solid state

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Abstract

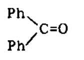
A number of mixed crystals, prepared by resolidification of a melt containing benzophenones and various hydrogen donors (molar ratio, usually 1:1), were found, on the basis of powder X-ray diffractograms and phase diagrams, to be a mixture of the crystallites of each component. The mixed crystals underwent photochemical hydrogen transfer in the solid state. Thus the mixed crystal of benzophenone and durene gave benzopinacol and a condensation product **4** as the major products, and that of benzophenone and benzhydrol gave benzopinacol in good yield, indicating that hydrogen transfer occurred at the interface between the component crystallites.

Keywords: Hydrogen abstraction; Benzophenones solid-state photoreaction; Mixed crystals

1. Introduction

During the course of our studies on solid state organic photochemistry [1–4], we have reported an intermolecular hydrogen abstraction reaction which occurs by UV irradiation of 4,4′-dimethylbenzophenone (**11**) crystals [5]. X-Ray crystallographic analysis of this compound indicates that the carbonyl group of one molecule is located close to the methyl group of a neighbouring molecule in the crystal lattice, so that the excited ketone can abstract a hydrogen atom from the neighbouring molecule to give a dimeric compound (**11** → **14**). There have been several reports on the photochemical hydrogen abstraction reactions which occur between two different organic molecules in mixed crystal systems [6–11]. These reports describe the spectroscopic studies of UV-irradiated systems consisting of an *N*-heteroaromatic compound, such as azanaphthalenes or acridine, doped (0.1 mol.%) in the single crystal of a hydrogen-donating compound, such as durene or fluorene.

However, with the exception of 4,4′-dimethylbenzophenone, little work has been carried out on the product analysis of photochemical hydrogen abstraction reactions in the solid state on a preparative scale. We have reported various photochemical bimolecular reactions in the solid state using mixed crystals prepared by melting–resolidification from a mixture of two different organic molecules [1–4]. In a typical example, we have shown that there are two classes of mixed crystals (one forming a molecular compound and the other a simple mixture of the microcrystals of the


$Ph_2C=O$

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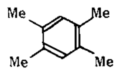

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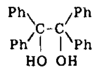

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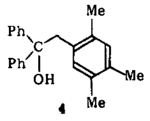

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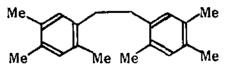

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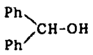

Ph_2CH-OH

6

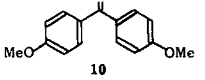
7

Ph_3CH

8

Ph_3COH

9



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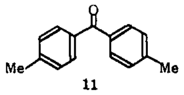

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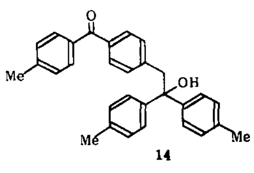

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components), and that photoreactions can occur in both classes [1–4].

The present report describes the photochemical behaviour of 1:1 mixed crystals between benzophenones and a hydrogen donor, focusing on the nature of the mixed crystals and the hydrogen abstraction process in the solid state.

2. Experimental details

2.1. General

Melting points (m.p.) are uncorrected and were measured with a JANACO MP-500D apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL PMX-60 spectrometer using tetramethylsilane as internal standard. Powder X-ray diffraction (PXD) patterns were taken on a Rigaku Geigerflex RAD-C system and differential scanning calorimetry (DSC) was carried out on a Rigaku differential scanning calorimeter DSC-8230D. Electron paramagnetic resonance (EPR) spectra were measured on a JEOL JES-RE2X spectrometer. High performance liquid chromatography (HPLC) was carried out with a Waters 600E system controller and a 991J photodiode array detector on a Bondasphere 5 μm C18-100A (3.9 mm × 15 cm) column with an oven temperature of 40 °C and a water–methanol gradient (40:60 to 0:100) at a flow rate of 1.0 ml min^{-1}, unless otherwise stated.

2.2. Preparation of mixed crystals

Mixed crystals between two different organic compounds were prepared by melting a mixture of a given molar ratio of the two compounds in a glass vial, followed by resolidification of the melt at room temperature, or in a refrigerator if necessary, and pulverization before characterization and UV irradiation.

2.3. Photoreaction of the mixed crystal between benzophenone (1) and durene (2) (2:1 molar ratio)

2.3.1. In the solid state

The 2:1 mixed crystal was pulverized to a fine powder in a mortar and the powder (1.0 g) was placed between two Pyrex disks (diameter, 9 cm) and irradiated in a Pyrex-built irradiation apparatus [12] under argon at 6 °C with a 400 W high-pressure mercury lamp for 24 h. The irradiated mixture was separated by preparative thin layer chromatography (TLC) with Merck 60F$_{254s}$ silica gel plates using a mixture of 10:1 hexane–ethyl acetate as eluent to give the following six fractions: (1) a mixture of benzophenone and durene (25–30 wt.%); (2) benzopinacol (**3**), m.p. 184–187 °C (22%); (3) compound **4** (20%); (4) durene dimer **5** (2%); (5) benzhydrol (**6**), m.p. 65–68 °C (a minute amount); (6) intractable polymers (30%–35%). Fraction 3 was obtained as a liquid which crystallized after a few days. Compound **4**, m.p. 73–81 °C: ^{1}H-NMR (CDCl$_3$) δ 1.50 (s, 1H, OH), 1.95 (s, 3H), 2.00 (s, 6H), 2.10 (s, 3H), 3.55 (s, 2H, CH$_2$), 6.35 (s, 1H, aromatic H), 6.80 (s, 1H, aromatic H), 7.0–7.5 (m, 10H, aromatic H); found: C, 87.20%; H, 7.60%; calculated for $C_{23}H_{24}O$: C, 87.30%; H, 7.65%. Fraction 4 crystallized to give durene dimer **5**, m.p. 132–136 °C: ^{1}H-NMR (CDCl$_3$) δ 2.20 (s, 18H, CH$_3$), 2.70 (s, 4H, CH$_2$), 6.90 (s, 4H, aromatic H); IR (KBr) 875, 1440, 1460, 1600, 2900, 3000 cm^{-1}. An authentic sample of durene dimer **5** was prepared by heating a mixture of durene (6.74 g), di-tert-butylperoxide (3.49 g) and tert-butyl alcohol (2 ml) at 160 °C for 14 h followed by separation of the product mixture by preparative TLC.

2.3.2. In acetonitrile solution

Benzophenone (0.112 g, 0.61 mmol) and durene (0.042 g, 0.31 mmol) were dissolved in acetonitrile (10 ml) and the solution was irradiated by the same lamp with argon bubbling at 6 °C for 1 h. The irradiated mixture was separated by preparative TLC as above to give the following five fractions: (1) a mixture of benzophenone and durene (25–30 wt.%); (2) benzopinacol (**3**) (20%); (3) compound **4** (17%); (4) durene dimer **5** (3%); (5) unidentified polymers (30%–35%).

2.3.3. EPR measurement in the solid state

The steady state EPR spectrum of the mixed crystal of benzophenone and durene (2:1) was measured at −100 °C during irradiation with a 500 W xenon lamp. The results are described in Section 3.

2.4. Photoreaction of the mixed crystal between benzophenone (1) and fluorene (7) in the solid state

The mixed crystal prepared from a mixture of benzophenone (0.546 g, 3.0 mmol) and fluorene (0.499 g, 3.0 mmol) was irradiated under the same conditions as above for 24 h. The irradiated mixture was analysed by HPLC to show that it consisted of more than 95% of the starting materials and four minor products including a trace amount of benzopinacol (**3**).

2.5. Photoreaction of the mixed crystal between benzophenone (1) and triphenylmethane (8)

2.5.1. In the solid state

The 3:2 mixed crystal prepared from a mixture of benzophenone (0.548 g, 3.01 mmol) and triphenylmethane (0.488 g, 2.0 mmol) was irradiated under the same conditions as above for 24 h. HPLC analysis of the irradiated mixtures showed that the reaction mixture consisted of the unreacted starting materials (70%), benzopinacol (**3**) (6%), triphenylmethanol (**9**) (4%) and several unidentified minor products.

2.5.2. *In acetonitrile solution*

A solution of benzophenone (0.081 g, 0.44 mmol) and triphenylmethane (0.075 g, 0.31 mmol) in acetonitrile (10 ml) was irradiated externally with a 400 W high-pressure mercury lamp for 16 h. HPLC analysis showed that the reaction mixture consisted of the unreacted starting materials (50%), benzopinacol (**3**) (25%) and triphenylmethanol (**9**) (4%) as the major components.

2.6. *Photoreaction of the mixed crystal between benzophenone (1) and benzhydrol (6) (1:1 molar ratio) in the solid state*

The mixed crystal was prepared from benzophenone (1.82 g, 10.0 mmol) and benzhydrol (1.84 g, 10.0 mmol). The mixed crystal was irradiated as above under argon at 4 °C for 24 h. The reaction mixture was analysed by HPLC (column: Waters Bondasphere 5 μm silica-100A, 3.9 mm × 15 mm; solvent, 95:5 hexane–ethyl acetate) showing that it consisted of benzophenone (**1**) (74% recovery), benzhydrol (**6**) (59% recovery) and benzopinacol (**3**) (35% yield).

2.7. *Photoreaction of the mixed crystal between 4,4′-dimethoxybenzophenone (10) and benzhydrol (6) (1:1 molar ratio) in the solid state*

The mixed crystal was prepared from 4,4′-dimethoxybenzophenone (0.49 g, 2.0 mmol) and benzhydrol (0.36 g, 2.0 mmol) and irradiated as above for 48 h. TLC analysis of the irradiated mixed crystal showed only the spot of the starting materials.

2.8. *Photoreaction of the mixed crystal between 4,4′-dimethylbenzophenone (11) and benzhydrol (6) (1:1 molar ratio)*

2.8.1. *In the solid state*

The mixed crystal was prepared from 4,4′-dimethylbenzophenone (1.05 g, 5.0 mmol) and benzhydrol (0.92 g, 5.0 mmol) and 300 mg of the mixed crystal was irradiated as above for 24 h. The irradiated mixture was analysed by HPLC using authentic samples as standards, showing that it consisted of **3** (8%), **12** (10%), **13** (4%), **1** (3%), **17** (2%), **14** (2%), recovered **11** (9%) and **6** (22%) and unidentified materials.

2.8.2. *In benzene solution*

A solution of a mixture of **11** (0.42 g, 2 mmol) and **6** (0.36 g, 2 mmol) in benzene (250 ml) was irradiated internally with a 100 W high-pressure mercury lamp with argon bubbling for 24 h. The irradiated mixture was evaporated to dryness and analysed by HPLC, showing that it consisted of **3** (20%), **12** (32%), **13** (22%), recovered **6** (11%) and unidentified materials.

2.9. *Phase diagrams of the mixed crystals*

The phase diagrams of the mixed crystals **1–6**, **10–6** and **11–6** were drawn using DSC data at different ratios of the components. The results are shown in Figs. 1(a)–1(c).

3. Results and discussion

3.1. *Preparation and characterization of mixed crystals*

The mixed crystals for solid state hydrogen abstraction were prepared by melting a 1:1 molar mixture of a benzophenone (**1**, **10** or **11**) and a hydrogen-donating compound (durene (**2**), fluorene (**7**), triphenylmethane (**8**) or benzhydrol (**6**)), followed by resolidification of the melt as described previously [1–4]. The mixed crystals thus prepared were characterized by PXD, DSC and IR spectroscopy. There are two major categories of mixed crystals: (1) the mixed crystal is a mixture of the microcrystals of each component; (2) the mixed crystal forms a polycrystalline molecular compound. Previous results have shown that the latter case often occurs with two different molecules having a similar molecular shape: such as indole and naphthalene [1] and carbazole and anthracene [13].

None of the mixed crystals listed in Table 1 formed a molecular compound. This conclusion was deduced from the fact that the PXD patterns of the mixed crystals were the same as the sum of those of the component compounds, except for the mixed crystal between 4,4′-dimethylbenzophenone (**11**) and benzhydrol (**6**). Although the mixed crystal **11–6** was thought to form a molecular compound due to the appearance of a few new peaks in its PXD pattern in comparison with those of the crystals of **11** and **6**, it showed a typical phase diagram (Fig. 1(a)) for a simple mixture of the crystallites of the two different compounds. The mixed crystals **1–6** and **10–6** also showed similar phase diagrams (Figs. 1(b) and 1(c)). Each mixed crystal showed a eutectic point at a lower temperature than the melting points of the component crystals: 39.7 °C for the mixed crystal **1–2** (2:1); 39.8 °C for **1–7** (1:1); 40.3 °C for **1–8** (1:1); 50.5 °C for **1–6** (1:1); 62.9 °C for **10–6** (1:1); 50.5 °C for **11–6** (1:1).

3.2. *Photochemistry of mixed crystals*

The solid state irradiation of the mixed crystals was carried out with a high-pressure mercury lamp under

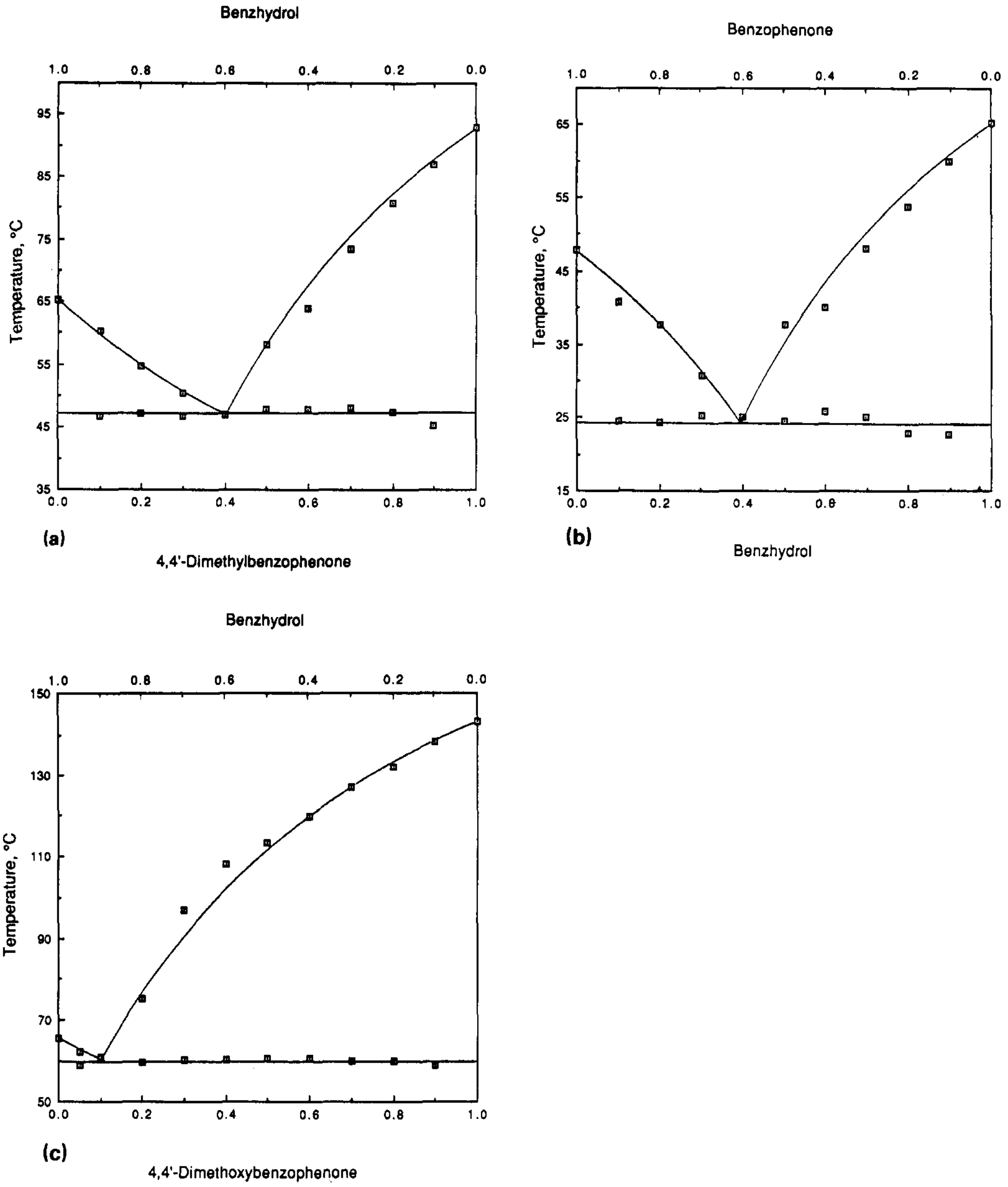


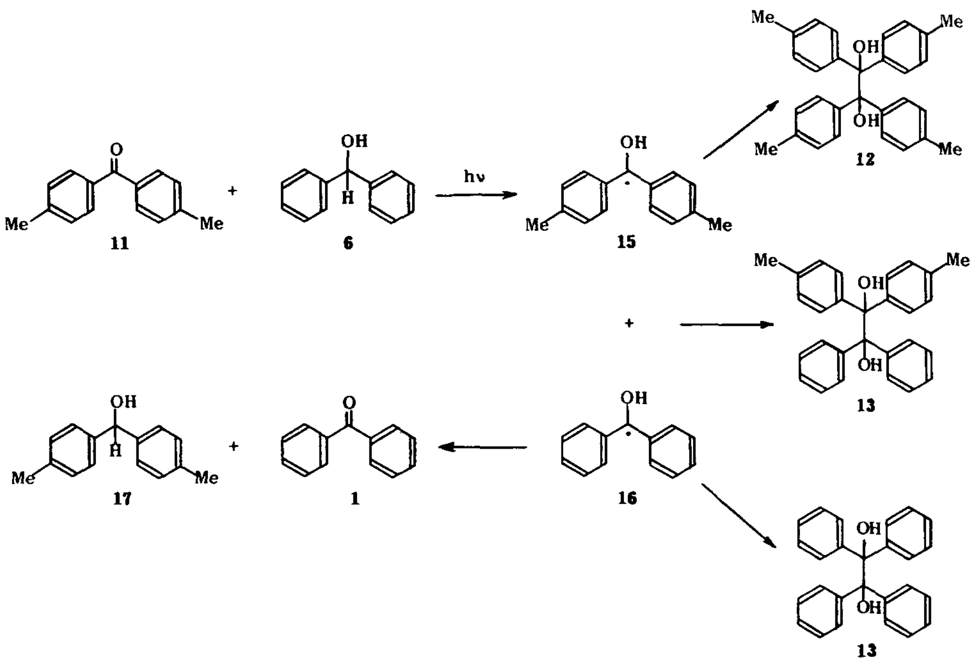
Fig. 1. Phase diagrams of the mixed crystals between 4,4'-dimethylbenzophenone (**11**) and benzhydrol (**6**) (a), benzophenone (**1**) and benzhydrol (**6**) (b) and 4,4'-dimethoxybenzophenone (**10**) and benzhydrol (**6**) (c). Numerals along horizontal axes denote fractions of components.

argon using a specially designed apparatus [12]. The photoproducts are listed in Table 1 and compared with those obtained in solution. Except for **1–7** and **10–6** mixed crystals, which showed no photoreactivity, benzophenones **1** and **11** underwent hydrogen abstraction from the counterpart hydrogen donors. The results indicate that the photoreactions occur at the interface of the crystallites of the two components, and that no significant difference between the solid state and solution phase is observed with regard to the distribution of the major products. The occurrence of an interface photoreaction has been reported previously for the solid state irradiation of mixed crystals between indole and phenanthrene [1], aromatic aldehydes and indole [3] and carbazole and *trans*-stilbene [4].

The major photoproducts from the mixed crystal **1–2** were, in addition to unidentified polymers, benzopinacol (**3**) and a coupling product **4** derived from the diphenylketyl and 2,4,5-trimethylbenzyl radicals which may be formed by hydrogen transfer between the excited benzophenone and durene. The product distribution in the photoreaction of **1** and **2** in acetonitrile solution was substantially the same as in the solid state. The mixed crystal **1–7** showed virtually no photoresistivity in the solid state. Benzopinacol (**3**) and triphenylmethanol (**9**) were obtained in the photoreaction of **1** and

Table 1
Photoreactions of benzophenone with hydrogen-donating compounds

Components of mixed crystals (molar ratio)	Photoproduct: % yield in the solid state (% yield in solution)
Benzophenone (**1**)/durene (**2**) (2:1)	**3**: 22 (20); **4**: 20 (17); **5**: 2 (3); **6**: trace (not determined); recovery: 25–30 (25–30); polymers: 30–35 (30–35)
Benzophenone (**1**)/fluorene (**7**) (1:1)	No reaction in the solid state
Benzophenone (**1**)/triphenylmethane (**8**) (3:2)	**3**: 6 (25); **9**: 4 (4); recovery: 70 (50)
Benzophenone (**1**)/benzhydrol (**6**) (1:1)	**3**: 35; recovery: **1**, 74; **6**, 59
4,4′-Dimethoxybenzophenone (**10**)/benzhydrol (**6**) (1:1)	No reaction in the solid state
4,4′-Dimethylbenzophenone (**11**)/benzhydrol (**6**) (1:1)	**3**: 8 (20); **12**: 10 (32); **13**: 4 (22); **1**: 3 (0); **17**: 2 (0); **14**: 2 (0); recovery: **11**, 9 (0); **6**, 22 (11)



Scheme 1.

8 in both the mixed crystal and acetonitrile solution. Triphenylmethanol (**9**) is probably formed by the autooxidation of an equilibrated mixture of the triphenylmethyl radical and hexamethylethane during the product separation process.

Whereas irradiation of the mixed crystal **1**–**6** gave benzopinacol (**3**) as a single product, the mixed crystal **10**–**6** showed no photoreactivity in the solid state. The photoreaction of the mixed crystal **11**–**6** was complex. As shown in Scheme 1, the hydrogen abstraction reaction of **11** from **6** will result in the formation of a pair of radicals (**15** and **16**) which will theoretically give pinacols **3**, **12** and **13**, the corresponding benzhydrol **17** of **11**, and benzophenone (**1**). Among the expected products, **3**, **12**, **13**, **1** and **17** were detected in the photoreaction of the mixed crystal **11**–**6**, and **3**, **12** and **13** in the photoreaction of a benzene solution of **11** and **6**. A dimer **14**, which is a product in the solid state photoreaction of **11** alone [5], was also detected among the photoproducts of the mixed crystal **11**–**6**.

The EPR spectrum of the mixed crystal **1**–**2** was measured during irradiation with a xenon lamp at − 100 °C. A broad unresolved EPR line with a g value of 2.0019 and a peak-to-peak width $B_{pp} = 1.2$ mT was observed, which can be assigned to the diphenylketyl radical (**16**).

4. Conclusions

All the mixed crystals between benzophenones (**1**, **10** and **11**) and hydrogen-donating compounds (**2**, **6**, **7** and **8**) were found to be a mixture of the crystallites of the components, and did not form a molecular compound. Photoreactions carried out in both mixed crystal form and in solution gave essentially the same products, which resulted from the initial hydrogen abstraction by the excited benzophenone molecule. The photochemical non-reactivity of the mixed crystals **1–7** and **10–6** is assumed to depend on the molecular arrangement near the surface of the component crystallites, although other interpretations may be possible. In these cases, the carbonyl oxygen and C–H hydrogen may not be arranged sufficiently close to each other to undergo hydrogen transfer at the interface.

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