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THE PHOTOREACTIONS OF SOME DIARYL ETHERS

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Abstract—Diphenyl ether, 1,4-diphenoxybenzene, and some substituted diaryl ethers have been irradiated in solution. The reactions observed are: (1) cleavage of the ether bond(s) followed by H-abstraction from the solvent yielding phenols and benzene derivatives, and (2) a photo-Claisen type rearrangement yielding 2- and/or 4-hydroxybiphenyl derivatives. The product distribution was found to depend on the solvent. The *o*/*p* ratio of rearrangement of diphenyl ether was found to be concentration dependent, the *o*-isomer increasing at the expense of the *p*-isomer on dilution.

INTRODUCTION

THE photoreactions of aryl ethers have been the subject of a number of papers. In 1952 Kharasch *et al.*[1] reported the photolysis of allyl phenyl, benzyl phenyl and diphenyl ether in i-propanol. According to this preliminary report, phenol and the *p*-rearranged phenol were formed exclusively. These observations are incorrect as in 1965 Bach and Barclay[2] reported that in addition to the products found by Kharasch *et al.* the *o*-rearranged phenol is also formed. More recently the photolysis of the above mentioned aryl ethers (with identical results) was reported by Kelly *et al.*[3] In the present paper our results on the photoreactions of some diaryl ethers in various solvents are reported.

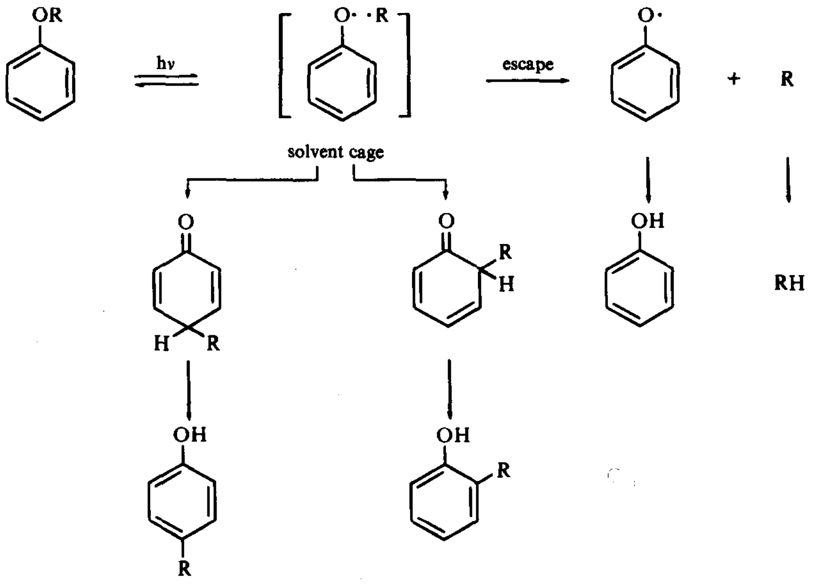
RESULTS AND DISCUSSION

All the diaryl ethers used in this study proved to be converted to a number of products on irradiation by the (unfiltered) UV light of a high pressure mercury lamp at 25°. It is reported,[4] however, that photolysis of diphenyl ether under 254 nm irradiation in i-propanol requires thermal activation (82°).

During the irradiations small aliquots were taken at regular intervals and analyzed by GLC. The conversion of the starting ethers as well as the product yield *vs* time plots proved to be linear through 20% conversion. Therefore, product distributions in various solvents were compared at 20% conversion of the starting ethers. The results thus obtained for diphenyl ether and 1,4-diphenoxybenzene are collected in Table 1. The results for the substituted diaryl ethers are collected in Table 3.

The photolysis proceeds at a higher rate in i-propanol than in ether. In benzene and cyclohexane (results not shown) the rate was too low to allow an accurate determination of the products. The consumed starting material was better accounted for in i-propanol than in ether. The gaschromatograms of the irradiation mixtures in ether showed a number of (minor) unidentified peaks, presumably reaction products with the solvent. It is also seen that the product distribution changes on going from i-propanol to ether.

All irradiation products can be rationalized on the basis of the mechanism postulated by Bach and Barclay.[2] They assumed a primary cleavage of the (aromatic)



ether bond(s) into two radical fragments held in a solvent cage. In the solvent cage the primary radicals either revert to starting ether or rearrange to the *o*- and/or *p*-substituted phenol, e.g. by an intramolecular process. Escape from the cage is followed by H-abstraction from the solvent* yielding the phenol and the benzene derivative.†

It was tried to obtain proof for such an intramolecular process in two ways. Firstly, no cross products could be detected on irradiation of diphenyl ether in the presence of either *o*- or *p*-cresol. Secondly, the photolysis of diphenyl ether was studied over the concentration range of $5 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ M in i-PrOH. The results are shown in Table 2.

A gradual increase in rate was observed on dilution. The ratio of rearranged products/phenol remained constant over the concentration range studied. It is noted, however, that on dilution the amount of *o*-rearranged product is increased at the expense of the *p*-rearranged product. A possible explanation for this might be that the *o*-isomer is formed by an entirely different process. One such a process could be the intermediary formation of dibenzofuran on irradiation of diphenyl ether and subsequent photolysis to *o*-phenylphenol. Although the formation of dibenzofuran

* This is, at least in the case of i-propanol being the solvent, indicated by the formation of considerable amounts of pinacol.

† No biphenyl could be detected.

Table 1 footnotes—

[a] The unfiltered light of a high pressure mercury lamp (Hanau TQ 81) was used throughout. Irradiations were carried out at 25° under N_2. All concentrations were 10^{-2} M.

[b] Product yields were determined by GLC and are expressed in mole % based on consumed starting material. In one case (diphenyl ether in i-PrOH) the benzene formed was determined quantitatively. It was formed in the same amount as phenol. The consumed ether is not completely accounted for due to the fact that some minor compounds remained unidentified. This was more pronounced in ether than in i-PrOH. Furthermore, some tar was also produced.

TABLE 1. THE IRRADIATION[a] OF DIPHENYL ETHER AND 1,4-DIPHENOXYBENZENE. PRODUCT YIELDS[b] AT 20% Conversion of Starting Material

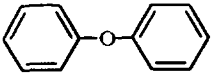
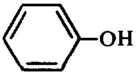
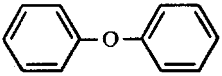
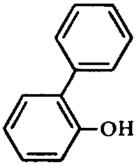
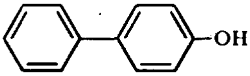
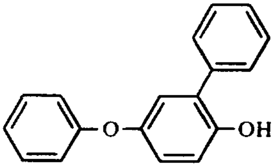
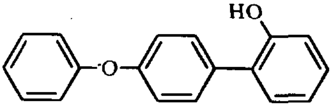
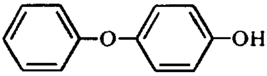
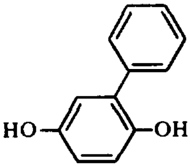
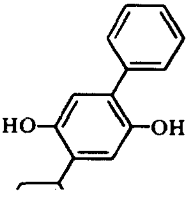
	Solvent				
		i-PrOH	Ether	i-PrOH	Ether
1		33·0	46·1	9·4	28·6
2		—	—	1·9	12·1
3		30·3	14·6	0·2	0·3
4		24·3	2·9	8·7	2·4
5		—	—	23·6	4·5
6		—	—	4·3	2·4
7		—	—	5·7	20·5
8		—	—	9·4	0·8
9		—	—	9·7	trace
10		—	—	trace	0·7

TABLE 2. THE IRRADIATION OF DIPHENYL ETHER IN i-PrOH. PRODUCT DISTRIBUTION[a] *vs* CONCENTRATION

Concn	Phenol	*o*-Phenylphenol	*p*-Phenylphenol	*o* + *p*/Phenol	*o*/*p*-Phenylphenol[b]
$5 \cdot 10^{-2}$	30·3	26·7	21·9	1·60	0·61
$2 \cdot 10^{-2}$	33·0	30·3	24·3	1·65	0·62
$5 \cdot 10^{-3}$	19·0	20·0	10·3	1·60	0·97

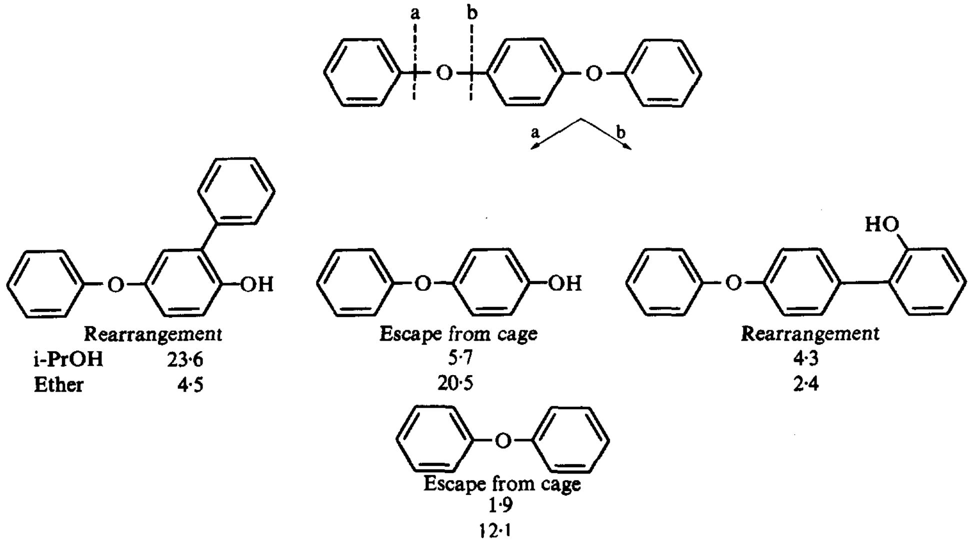
[a] Product yields (mole %) are based on consumed starting material (20% conversion).

[b] Allowance is made for the availability of two *o*-positions and only one *p*-position.

on irradiation of diphenyl ether has been reported by Stegemeyer[5] we have not been able to detect this compound at any stage of the photolysis. Joschek and Miller[6] have also looked in vain for dibenzofuran on irradiation of some phenoxyphenols. Moreover, dibenzofuran proved to be stable on irradiation in i-PrOH as well as in ether. On these grounds this process can be discounted. Alternatively, the *o*-rearrangement might be some sort of concerted process.† The rearrangement to the *p*-position, however, requires the aryl moiety to get round to the other side of the ring. The possible influence of concentration on such a process is not clear at present. A study of optically active ethers e.g. α-methylbenzyl phenyl ether might provide some more information.

The change from i-PrOH to ether means approximately a twenty-fold decrease in viscosity. This can be expected to lead to a higher proportion of escape from the solvent-cage. This would result in a higher proportion of phenol relative to the total of rearranged products. The ratio of rearranged products to phenol indeed decreased from 1·65 (i-PrOH) to 0·38 (ether). The *o*/*p* ratio of rearranged products increased from 0·62 (i-PrOH) to 2·52 (ether).

In the case of 1,4-diphenoxybenzene a similar effect is observed. There are two



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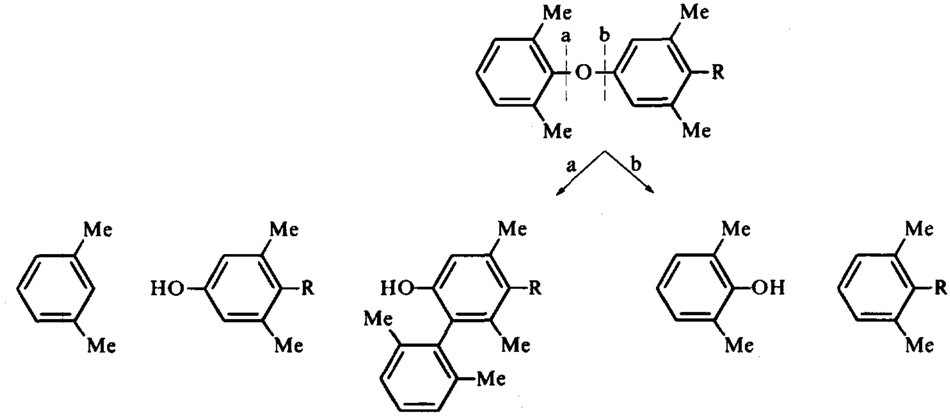
* In the light of this result it is questionable whether the observed *o*/*p*-ratio can be correlated with calculated unpaired electron densities in the phenoxy radical.[4]

† For the photo-Fries rearrangement (to the *o*-position) of *p*-methoxyphenyl acetate[7] and *p*-tolyl acetate[8] respectively a concerted process has been suggested.

modes, path (a) and path (b) for the first ether-bond cleavage. It is readily seen that the ratio of rearrangement to "escape from the cage" again decreases on going from i-PrOH to ether. It is not possible to extend this comparison to the further irradiation products, since most of these products can be formed in a number of ways.

Two other diaryl ethers, 4-(2,6-dimethylphenoxy)-2,6-dimethylanisole and 4-(2,6-dimethylphenoxy)-1,2,6-trimethylbenzene have also been irradiated in different solvents. Again, irradiation products were found resulting from (aromatic) ether-bond cleavage and subsequent H-abstraction and/or rearrangement (see Table 3). Owing to the unsymmetrical substitution pattern in the starting ethers, two modes of ether-bond cleavage are possible. From the characterized products it can be concluded that in the case of the anisole (R = OMe) both modes occur. However, in the case of the other diaryl ether (R = Me) we must conclude that the ether bond is cleaved specifically (path a).* It does not make sense to discuss a possible solvent influence in the case of these two diaryl ethers since only a very small number of irradiation products have been isolated and identified.



R = OMe	+	+	+	+	+
R = Me	?	+	+	−	−

EXPERIMENTAL

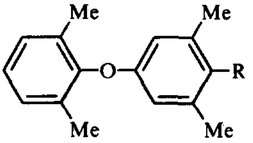
Materials. Diphenyl ether used in this study was purchased (Fluka) and used as received. 1,4-Diphenoxybenzene† was prepared by an Ullmann coupling of 4-bromodiphenyl ether and phenol, b.p. 170°/0·8 mm, m.p. 71–71·5° (EtOH). 4-(2,6-Dimethylphenoxy)-2,6-dimethylanisole‡ was prepared by an Ullmann coupling of 4-bromo-2,6-dimethylanisole and 2,6-dimethylphenol, m.p. 58·5–59·3° (MeOH), reported[9] m.p. 57·5–58·5°. Demethylation of this ether and esterification with Ac_2O in pyridine led to 4-(2,6-dimethylphenoxy)-2,6-dimethylphenyl acetate, m.p. 123–124° ($AcOH$-H_2O). Irradiation of this acetate[10] in ether (10^{-2} M) gave 4-(2,6-dimethylphenoxy)-1,2,6-trimethylbenzene, which was isolated from the irradiation mixture by chromatography (silica gel: light petroleum-ethyl acetate 99:1), m.p. 96·5–97·5°.

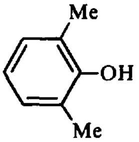
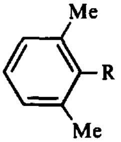
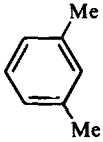
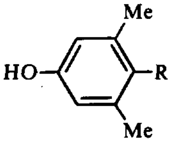
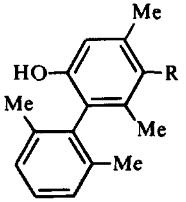
* Although we have characterized only two of the irradiation products, we could not have overlooked 1,2,3-trimethylbenzene nor 2,6-dimethylphenol both "path b"-products since both compounds are readily recognised by GLC and TLC.

† This compound was prepared by Mr. C. H. R. I. de Jonge.

‡ This compound was prepared by Mr. C. A. M. Hoefs.

TABLE 3. THE IRRADIATION[a] OF TWO SUBSTITUTED DIARYL ETHERS. PRODUCT YIELDS[b] AFTER AN 8 H IRRADIATION PERIOD.



		R = OMe		R = Me	
	Solvent	Benzene	Ether	Dioxane	Ether
	Conversion (%)	20·0	51·0	92·4	97·1
1		26·9	12·7	—	—
2		trace	1·5	—	—
3		3·8	60·5	—	—
4		trace	13·2	13·1	13·6
5		4·4	4·1	13·5	2·6

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[a] See Table 1.

[b] Product yields were determined by GLC and are expressed in mole % based on consumed startin material

Irradiation procedure. A cylindrical vessel (150 ml), double-walled for cooling and fitted with a reflux condenser, a gas inlet tube, a magnetic stirrer and a thermometer was used. The unfiltered light of a high pressure Hg lamp (Hanau TQ 81) was used throughout. In all cases the solns of the ethers were flushed with N_2 before and during the irradiation. A temp of 25° was maintained in all irradiation experiments.

Isolation and identification of products. 2-Phenyl-4-phenoxyphenol (compd 5, Table 1) was isolated from the irradiation mixture of 1,4-diphenoxybenzene in i-PrOH. After a preseparation (silica gel: benzene-EtOAc 99:1) the product was isolated by preparative GLC (Varian Aerograph model 700, single column, hot wire detector). A 7 ft long and $\frac{1}{4}$ in. o.d. stainless steel tubing packed with 10% (w/w) silicon gum rubber S.E. 30 on chromosorb W 60/80 mesh was used (column temp 200°; detector and injector temp 225°; carrier gas H_2: 60 ml/min). The structure was elucidated by means of spectroscopic methods.

IR: monosubstitution, 700 cm^{-1} (2 bands); 1,2,4-trisubstitution, aromatic C—O—C, 725 cm^{-1}; internally associated OH, 3560 cm^{-1}.

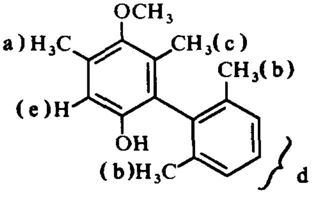
NMR: 7·28 ppm, singlet (5H: phenyl ring); 6·73–7·28 ppm, 2 multiplets (5H: phenoxy ring and 3H: central ring) and 4·90 ppm, singlet (1H: OH group).

The existence of 2-hydroxy-4′-phenoxybiphenyl (compd 6, Table 1) in the irradiation mixture of 1,4-diphenoxybenzene was concluded from the following facts (1) the R_f values of **5** and **6** are the same on TLC in a number of solvent systems, (2) combined GLC/TLC gives two peaks (resolution 60%) and the 2 spots on TLC next to each other with the same R_f value[11] in benzene-EtOAc 9:1.

The existence of 2,5-diphenylhydroquinone (compd 10, Table 1) in the irradiation mixture of 1,4-diphenoxybenzene was concluded from the following facts: 1° after silylation of the irradiation mixture with bis-trimethylsilylacetamide (BSA)[12] and combined GLC/TLC (TLC elution with benzene-EtOAc 9:1 after desilylation on the plate with HCl gas during 1–3 sec) the R_f values of hydroquinone, phenylhydroquinone and compd 10 are 0·12, 0·23 and 0·37 respectively (nearly a straight line with a slope of 45°), and 2° GLC/TLC without silylation gives yellow quinone spots on TLC.

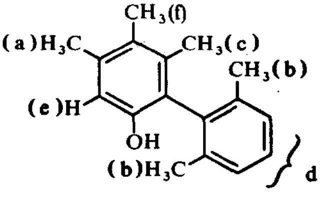
2,6-Dimethyl-4-hydroxyanisole (compd 4, Table 3, R = OMe) and 6-hydroxy-3-methoxy-2,4,2′,6′-tetramethylbiphenyl (compd 5 Table 3, R = OMe) were isolated from the irradiation mixture of 4-(2,6-dimethylphenoxy)-2,6-dimethylanisole in ether by column chromatography. Eluent for compd 4: light petroleum-EtOAc 99:1. The isolated product had m.p. 84–84·5° (reported m.p. 84–85°). The structure was supported by IR and NMR. Eluent for compd 5: light petroleum-EtOAc 99:1 followed by a second column isolation using CCl_4–MeOH 99:1. The isolated product had m.p. 120·5–121·5°. The structure followed from IR and NMR data:

IR: 1,2,3,4,5-penta-substitution 860 cm^{-1}, 1,2,3-tri-substitution 725 cm^{-1}, OMe stretching (sym) 2830 cm^{-1}, internally associated OH 3550 cm^{-1}.



NMR: 1·80 ppm, singlet (3H: a); 1·97 ppm, singlet (6H: b); 2·27 ppm, singlet (3H: c); 3·63 ppm, singlet (3H: OMe); 4·03 ppm, singlet (1H: OH); 6·60 ppm, singlet (1H: e); and 7·12 ppm singlet (3H: d).

3,4,5-Trimethylphenol (compd 4 Table 3, R = Me) and 2,3,4,2′,6′-pentamethyl-6-hydroxybiphenyl (compd 5, Table 3, R = Me) were isolated from the irradiation mixture of 4-(2,6-dimethylphenoxy)-2,2,6-trimethylbenzene in dioxane by column chromatography. Eluent for compd 4: benzene-EtOAc 98:2. The structure of the product followed from its IR (identical with Sadtler no 296) and NMR spectrum. Eluent for compd 5: light petroleum-EtOAc 99:1. The isolated product had m.p. 79–81°. Its structure followed from IR and NMR data:



IR: 1,2,3,4,5-penta-substitution 860 cm^{-1}; 1,2,3-tri-substitution 725 cm^{-1}; internally associated OH 3550 cm^{-1}.

NMR: 1·82 ppm, singlet (3H: a); 1·97 ppm, singlet (6H: b); 2·13 ppm, singlet (3H: f); 2·27 ppm, singlet (3H: c); 3·92 ppm, singlet (1H: OH); 6·60 ppm, singlet (1H: e) and 7·10 ppm, singlet (3H: d).

All other products were commercially available and were used after purification by fractionation and/or crystallization.

Quantitative analysis. Samples were drawn from the irradiation mixtures at regular intervals. The quantitative results were obtained by GLC (Varian Aerograph model 1520-B, dual column, dual flame ionization detection). For the separation of the reaction products of diphenyl ether, 4-(2,6-dimethylphenoxy)-2,6-dimethyl-anisole and 4-(2,6-dimethylphenoxy)-1,2,6-trimethylbenzene a 7 ft and ⅛ in. o.d. stainless steel column packed with 15% silicon gum (nitrile) XE-60 on 60/80 mesh Diatoports S (HMDS-treated) was used (column temp 70–220°, program rate 10°/min, injector and detector temp 270°, carrier gas N_2*). Sulfolane† was used as an internal standard.

For the separation of the reaction products of 1,4-diphenoxybenzene a different procedure was followed. First of all the samples were all silylated in bulk with BSA before injection. Because the separation of a number of products proved to be difficult on a packed column, a 90 ft and 0·01 in. i.d. stainless steel open tubular column‡ coated with Apiezon L was used. The following coating procedure was followed: 100 mg of hexadecyltrimethylammonium bromide was added to 50 ml of a 15% solution of Apiezon L in $CHCl_3$, according to Metcalfe and Martin;[14] 5 ml of this soln was pressed through the column (2 atm). After the $CHCl_3$ was evaporated (2 h at 25° and 2 atm) the column was finally heated at 260° during 3 hr. The column was used under the following conditions: column temp 90–255°; injector and detector temp 275°; program rate 8°/min; flow rate from 90 to 255°: 3·3 ml/min with an inlet pressure of 20 psi. At the end of the temp range flow programming was employed. The inlet press was programmed from 20 to 64 psi in 7 min. In this way the total analysis time was shortened from 42 to 27 min. Split ratio 1:30. Yields were calculated from the peak areas taking into account the Area Correction Factors of the respective compounds.

Acknowledgement—The assistance of Mr. J. P. van Klaveren in part of the experimental work is gratefully acknowledged. The IR and NMR spectra were recorded by Mr. H. Kenemans under the supervision of Dr. W. G. B. Huysmans.

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* The carrier gas was led through a stainless steel vessel filled with silica gel-H_2O 1:1 (w/w). After passing this vessel the N_2 contains a constant % of H_2O throughout the chromatographic system to prevent undesirable irreversible adsorption of phenols to the solid support and/or the stationary phase.

† Sulfolane was found to be photochemically stable.[13]

‡ Reasonable agreement between the quantitative results (diphenyl ether) obtained on the packed column and those obtained on the open tubular column was observed.

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