[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

THE FORMATION OF DIMERIC PEROXIDES BY OZONIZATIONS OF OLEFINS (1)

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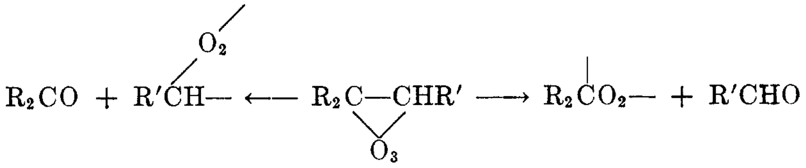
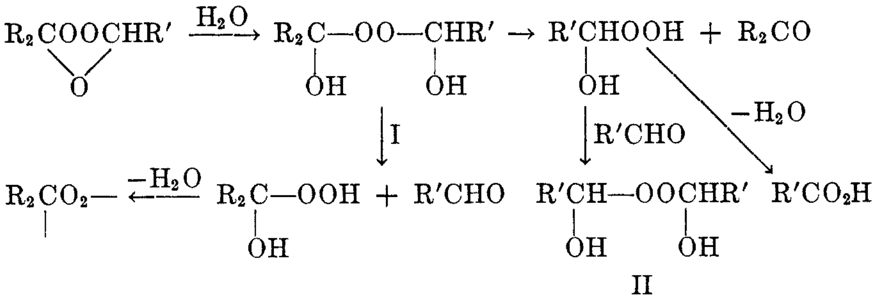
The formation of dimeric diaryl ketone peroxides during the ozonization of arylated olefins (1) has led us to believe that peroxides are to be expected as products of the decomposition of any ozonide. An unsymmetrical olefin ozonide may cleave in either of two ways, and the products isolated



from the ozonolysis mixture will be dependent on the manner in which these possible intermediates dimerize or rearrange. This view is very strongly supported by the work of Briner and his co-workers (2).

Rieche (3) has accounted for the formation of the various products obtained in ozonolysis on the basis of a hydrolytic cleavage which is outlined below

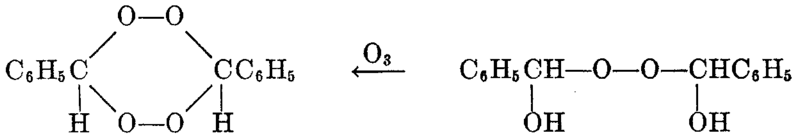


The principal difference between these two schemes for the breakdown is that Rieche believes a dihydroxy peroxide (I) is an intermediate in the formation of the final products whereas the other mechanism does not postulate hydrolysis. Both points of view have supporting evidence in the literature. Perhaps one of the strongest arguments for the Rieche mechanism of cleavage is the occasional isolation of the symmetrical dihydroxy peroxide (II).

In studying the ozonization of various arylated olefins we have secured evidence which we believe supports the former mechanism of ozonide cleavage.

Ozonization of arylated olefins under a wide variety of conditions has shown that approximately the same amount of peroxide is formed from a given olefin whether the ozonization mixture is treated with water or worked up under anhydrous conditions. Ozonization was even carried out in solutions which contained suspended anhydrous copper sulfate to detect the presence or the formation of water and in spite of the apparent absence of water the peroxides were formed as usual.

Ozonolysis of styrene, stilbene, and triphenylethene has in each case yielded the known dimeric benzaldehyde peroxide (4) (III), although this peroxide does not appear to have been previously obtained from an ozonolysis reaction of this type (5). We thought the dimeric benzaldehyde peroxide might be formed by the dehydrogenation by ozone of the corresponding dihydroxydibenzal peroxide (6) (IV) which could be present as a result of complex changes of the type suggested in Rieche's scheme of breakdown of the ozonide. Actually ozonization of dihydroxydibenzal peroxide does give low yields of dimeric benzaldehyde peroxide (III) but this does not seem to be the course of the latter in our ozonolysis experiments on styrene, stilbene, and triphenylethene. Attempts were made to isolate the easily characterized dihydroxydibenzal peroxide from styrene and stilbene ozonolysis products but none could be found. That the product of styrene ozonolysis is not sensitive to water was shown by allowing a sample of the styrene ozonide in carbon tetrachloride to stand for two days with water without any evident changes in its properties. Briner and Gelbert (5) have also observed the stability of styrene ozonide towards water.



III IV

Treatment of dihydroxydibenzal peroxide with phosphorus pentoxide gave some dimeric benzaldehyde peroxide. It was therefore thought that treatment of the ozonolysis mixture of 1,1-diphenylethene and 1,1-diphenylpropene-1 with phosphorus pentoxide (3) would increase the amount of dimeric benzophenone peroxide if an intermediate such as (I) were formed by hydrolysis of the ozonide. No such increase in dimeric benzophenone peroxide resulted from this treatment.

An attempt to convert dihydroxydibenzal peroxide into stilbene ozonide by dehydration with phosphorus pentoxide was inconclusive. No evidence of ozonide formation was obtained. Yet the products actually isolated from the mixture were identical with those isolated by the decomposition of stilbene ozonide (7).

According to the view that ozonides cleave spontaneously in two directions, it would be logical to assume that the proportion of cleavage in either direction would be influenced by the nature of the substituents on the olefin. That this actually is the case is shown by the yields of peroxides obtained from various arylated olefins. With diarylated compounds of the type $(C_6H_5)_2C{=}CHR$ the yield of dimeric benzophenone peroxide is 4–5% when $R = H$ and 12% when $R = n\text{-}C_2H_5$. When R is phenyl, although a further increase in the yield of dimeric benzophenone peroxide results, dimeric benzaldehyde peroxide is formed simultaneously. This mixture cannot be separated readily. Tetraphenylethylene on ozonolysis gives 53–57% yields of dimeric benzophenone peroxide calculated on the basis that only one molecule of the peroxide can form from one molecule of the olefin.

These results are of some significance in connection with certain ozonolysis reactions which have been suggested as analytical procedures. For example, ozonolysis has been used (8) to convert terminal $=CH_2$ groups to formaldehyde for quantitative determination. Our results indicate that the groups attached to the second carbon of the olefin residue may have a marked effect on the ratio of formaldehyde to formic acid which is produced from the terminal $=CH_2$ group and hence influence the results. Thus we add one more bit of evidence to support Briner's view (9) that this method cannot be expected to give quantitative results.

The list of dimeric diaryl ketone peroxides which have been characterized has been extended to include dimeric *p,p'*-dichlorobenzophenone peroxide and dimeric di-*o*-tolyl ketone peroxides. Evidence for the existence of dimeric di-(3,4-dimethylphenyl) ketone peroxide as an ozonolysis product of 1,1-(di-3,4-dimethylphenyl)ethene has been obtained. Dimeric *p*-methoxyphenyl methyl ketone peroxide has also been characterized (10).

Dimeric benzophenone and di-*p*-tolyl ketone peroxides have now been synthesized from the corresponding ketones and hydrogen peroxide but the oxidation takes several months. This indicates that the peroxides isolated in ozonolysis of olefins do not result from oxidation of ketones by hydrogen peroxide formed by hydrolysis of the ozonides.

A most surprising result was that ozone oxidized benzaldehyde to give a 15% yield of benzoyl peroxide. Earlier investigators (11) obtained benzoic acid and perbenzoic acid by this reaction. Rupe and Hirschmann (12) did not obtain benzoyl peroxide by the ozonization of benzoic acid and we have likewise failed to do so. Hence, benzoic acid is apparently not an intermediate between benzaldehyde and benzoyl peroxide.

EXPERIMENTAL

Dimeric benzaldehyde and benzophenone peroxides through ozonlysis. Representative experiments in the production of dimeric benzaldehyde and benzophenone peroxides from the ozonolysis of olefins in various solvents with changes in temperatures and times of ozonization are shown in Table I. For this work a concentration of

TABLE I

BENZALDEHYDE AND DIMERIC BENZOPHENONE PEROXIDES FROM THE OZONOLYSIS OF OLEFINS

ALKENE	AMOUNT, G.	SOLVENT	CONDITIONS OF OZONIZATION			YIELD OF PEROXIDE	
			Volume, cc.	Temperature	Time, min.	Grams	Per cent
Styrene	5.0	CCl_4	60	Room	120	0.095	1.7[a]
Stilbene	2.0	C_6H_6	50	"	120	.13	9.6[b]
1,1-Diphenylethene	3.0	n-C_6H_{14}	40	Ice-salt	25	.19	5.8[c]
"	4.0	"	40	"	30	.20	4.5[c]
"	4.0	C_6H_{12}	40	"	35	.24	5.5[c]
"	3.1	CCl_4	40	"	30	.17	5.0[c]
"	3.0	$CH_3CO_2C_2H_5$	30	"	30	.045	1.4[c, d]
"	3.0	CH_3CO_2H	35	20°	30	.03	0.9[c, d]
1,1-Diphenyl-1-butene	2.65	CCl_4	75	Room	300	.4	12.0
Triphenylethene	4.7	CCl_4	40	Ice-salt	45	1.275 (mixture of two not separated)[e]	
"	3.0	$CHCl_3$	75	−40 to −60°	110	0.658	"
"	3.0	C_2H_5Cl	65	−60°	120	1.134	" [e, f]
"	2.5	"	40	−50 to −60°	40	0.975	" [e, g]
Tetraphenylethene	1.9	CCl_4	125	Ice	80	.645	57.0
"	2.0	CCl_4	125	Ice	120	.634	53.0

[a] The dimeric benzaldehyde peroxide melted at 200° with gas evolution and when mixed with a sample of the peroxide prepared by the method of Baeyer and Villiger (4) there was no depression in the melting point.

[b] From the filtrate after isolation of the peroxide, 0.71 g. of benzoic acid was isolated.

[c] The solvent was removed in a vacuum desiccator after ozonization and the peroxide separated with absolute alcohol.

[d] This mixture was still strongly unsaturated towards bromine in carbon tetrachloride after the peroxide had been isolated.

[e] This mixture of dimeric benzophenone and benzaldehyde peroxides melted with gas evolution at about 184°. Benzoic acid was also isolated. The characteristic fragrant odor of crude benzaldehyde peroxide was noted.

[f] Ozonization was continued for about sixty minutes after the appearance of the blue color in the reaction-mixture.

[g] Ozonization was stopped at the first appearance of the blue color.

ozone of 2.5–3.5% and a rate of gas flow of about 18 l. per hour were used. In some experiments ozonizations were continued for thirty to ninety minutes after the appearance of a blue color in the solvent, which was assumed to indicate saturation of the olefin bond with ozone. In others, the mixture of products remaining after separation of the peroxide contained unchanged olefin. In some cases the ozonides were decomposed in the presence of water and the acidic products removed by alkaline extraction; in others, the solvents were removed in a vacuum desiccator and the peroxides separated by virtue of their insolubility in absolute alcohol or ether.

In Table II are shown the yields of peroxides isolated from ozonides which had been treated in carbon tetrachloride solution with phosphorus pentoxide at about 5° for various periods of time prior to aqueous or anhydrous decomposition. The yield from an anhydrous decomposition of the ozonide from 1,1-diphenyl-1-propene which had not been treated with phosphorus pentoxide is included for comparison.

Aqueous decomposition of dihydroxydibenzal peroxide. A suspension of 0.5 g. of dihydroxydibenzal peroxide in 25 cc. of ozone-saturated carbon tetrachloride was treated with 40 cc. of water for fifteen hours and extracted with alkali. The only product isolated was benzoic acid (0.015 g.). From a similar suspension which was treated with 15 cc. of 30% hydrogen peroxide for eighteen hours 0.075 g. of benzoic acid was isolated.

TABLE II

TREATMENT OF OZONIDES WITH PHOSPHORUS PENTOXIDE

ALKENE	AMOUNT, G.	TIME OF OZONIZATION, MINUTES	TREATMENT WITH P_2O_5	YIELD OF PEROXIDE	
				g.	%
1,1-Diphenylethene	5.0	60	4–5 days[a]	0.18	3.3
1,1-Diphenyl-1-propene	4.0	25	13 hours[b]	.135	2.8
1,1-Diphenyl-1-propene	2.5	180	4 hours[a]	.12	4.0
1,1-Diphenyl-1-propene	4.5	25	—[b]	.16	3.5

[a] Wet isolation of peroxide.
[b] Dry isolation of peroxide.

Attempted detection and removal of water formed during ozonization. A solution of 3 g. of styrene in 50 cc. of dry carbon tetrachloride containing a suspension of 0.1 g. of anhydrous copper sulfate was ozonized for one hour and forty minutes in a train in which ingoing and outgoing gases passed through concentrated sulfuric acid. The copper sulfate showed no visible change. The solution was decanted through glass wool *via* a ground-glass joint into a second bottle in the train and subjected to vacuum evaporation under anhydrous conditions. There remained a red viscous residue, from which by treatment with dry ether was separated dimeric benzaldehyde peroxide as dirty white needles, melting with gas evolution at 183–193°, and a red amorphous product not melting below 350°. Other ozonizations carried out over anhydrous copper sulfate gave similar results. One sample exploded harmlessly during evaporation *in vacuo* when it became too warm; dimeric benzaldehyde peroxide was identified in the residue.

Attempted isolation of dihydroxydibenzal peroxide from the decomposition of styrene ozonide. A solution of 3.5 cc. of styrene in 50 cc. of carbon tetrachloride was ozonized for two hours with ice-salt cooling. The solvent was removed *in vacuo* at room temperature under a carbon dioxide atmosphere, and the residue was washed by decantation with dry hexane. It was then treated with 0.5 cc. of water in 10 cc. of anhydrous ether for two hours, during which time a slow evolution of gas was perceptible. By fractional crystallization only benzoic acid and benzaldehyde peroxide were isolated. No indication of the presence of dihydroxydibenzal peroxide was observed. Other ozonizations in carbon tetrachloride and hexane with ice-salt or acetone-dry ice cooling gave similar results. In one instance the oily filtrate remaining from the isolation of benzoic acid and benzaldehyde peroxide reacted vigorously with dilute solutions of sodium bisulfite or sodium hydroxide, probably due to the presence of undecomposed ozonide.

p,p′*-Dichlorobenzophenone peroxide.* 1,1-Di-*p*-chlorophenylethene was prepared by dehydrating with dilute sulfuric acid the carbinol obtained from methylmagnesium iodide and *p,p′*-dichlorobenzophenone. A product melting at 85–87° (lit. 91–92°) after recrystallization from methanol was used for ozonization.

A solution of 6.5 g. of the ethene in 100 cc. of carbon tetrachloride was ozonized for two and one-half hours with acetone-dry ice cooling. At this time saturation of the olefin bond was indicated by the blue color of ozone in the carbon tetrachloride solution. The mixture was decomposed with a solution of hydrogen peroxide and the acidic products were removed with dilute sodium hydroxide. *p*-Chlorobenzoic acid, m.p. 240° (lit. 236°, 243°) and oxalic acid, precipitated as calcium salt in acetic acid solution, were isolated from the alkaline extract. The residue from the carbon tetrachloride solution was dissolved in acetone and cooled. *p,p′*-Dichlorobenzophenone crystallized. The filtrate, concentrated and again cooled, gave 0.31 g. (4.5%) of *p,p′*-dichlorobenzophenone peroxide, which after recrystallization from acetone melted with gas evolution at 217.5–218.5°.

Anal. Calc'd for $C_{26}H_{20}Cl_4O_4$: C, 58.45; H, 3.02.
Found: C, 58.62; H, 3.08.

The product remaining after evolution of gas from the peroxide had ceased melted at 144–145° and a mixed melting point with an authentic sample of *p,p′*-dichlorobenzophenone, m.p. 147–148°, showed no depression.

*Di-*o*-tolyl ketone peroxide.* Difficultly separable liquid mixtures containing 1,1-di-*o*-tolylethene were obtained by dehydrating the addition-product from *o*-tolylmagnesium bromide and ethyl acetate. A fraction of 5.9 g. of impure ethene, boiling at 125–127° (4 mm.) n_D^{20} 1.5854, in carbon tetrachloride solution was ozonized for three and one-fourth hours and decomposed by the usual aqueous treatment. Alkaline extraction gave 1.09 g. of a mixture of solid acids, from which was isolated by solution in hot water 0.23 g. of *o*-toluic acid, melting at 90–99°, and 0.54 g. of a light yellow acid, insoluble in hot water, melting at 157°, N.E. 252, which was not further identified. By concentration of the carbon tetrachloride solution and addition of alcohol impure di-*o*-tolyl ketone was obtained, m.p. 65–72° (lit. 72°). After several months standing, the filtrates from several ozonolysis mixtures yielded about 0.035 g. of very impure peroxide, which melted with gas evolution at 175–180°. The amount of purified product, m.p. 183° was not sufficient for an analysis.

Ozonolysis of 1,1-(di-3,4-dimethylphenyl)ethene. 1,1-(Di-3,4-dimethylphenyl)-ethene was prepared essentially according to the directions of Bistrzycki and Reintke (13).

A 2.5 g. sample of the ethene in 60 cc. of carbon tetrachloride was ozonized for two hours and forty minutes with ice-salt cooling. On working up the ozonization mixture in the usual manner there was obtained chiefly di-(3,4-dimethylphenyl) ketone, m.p. 140°, plus a small amount of 3,4-dimethylbenzoic acid, m.p. 165.5–166°, N.E.

153 (calculated 150), and some oxalic acid. The more impure ketone fractions melted with slow evolution of gas to a temperature of 190°. However, when recrystallized these gave either the ketone or a product melting at 164–165° without gas evolution. The quantities of the latter compound were too small for further investigation. Other ozonolysis mixtures gave similar results.

Synthesis of dimeric diaryl ketone peroxides from the ketones and hydrogen peroxide. Dimeric benzophenone peroxide. A mixture of 0.55 g. of benzophenone and 30% aqueous hydrogen peroxide was allowed to stand two months. The crystalline material was separated and after digestion with alcohol 0.003 g. (0.5%) of dimeric benzophenone peroxide, m.p. 212.5°, remained undissolved.

A solution of 0.5 g. of benzophenone in 15 cc. of dry ethereal hydrogen peroxide, which was prepared by extracting 30% aqueous hydrogen peroxide with an equal volume of ether and drying the ethereal solution over anhydrous sodium sulfate, was allowed to stand for two months. A few crystals of dimeric benzophenone peroxide, melting and evolving gas at about 212.5°, were isolated.

*Di-*p*-tolyl ketone peroxide.* A mixture of 0.5 g. of di-*p*-tolyl ketone and 20 cc. of 30% hydrogen peroxide was let stand two months and filtered. Digestion of the solid material with ethyl alcohol left 0.004 g. (0.8%) of dimeric di-*p*-tolyl ketone peroxide, melting at 202–205°, undissolved.

A solution of 0.5 g. of di-*p*-tolyl ketone in dry ethereal hydrogen peroxide was let stand two months and the solvent evaporated. The residue gave 0.005 g. (1%) of dimeric di-*p*-tolyl ketone peroxide, melting above 195° with gas evolution.

Attempted synthesis of dimeric di-(3,4-dimethylphenyl) ketone peroxide. A mixture of 0.5 g. of di-(3,4-dimethylphenyl) ketone and 20 cc. of dry ethereal hydrogen peroxide was allowed to stand for three months. The solvent was evaporated and the residue fractionally crystallized from acetone. The last two of five fractions melted at about 130° with gas evolution to 170°. Recrystallization of these fractions gave similar results, but no ketone peroxide could be isolated.

Dimeric p*-methoxyphenyl methyl ketone peroxide.* 1-*p*-Methoxyphenyl-1-methylethene was prepared by dehydrating the product obtained from the addition of methylmagnesium iodide to methyl anisate (10), with 10% sulfuric acid. Since considerable polymerization occurred during fractional distillation of the ethene under 15 mm. pressure, impure samples were used for ozonization.

A 3.8 g. sample of 1-*p*-methoxyphenyl-1-methylethene, n_D^{20} 1.5665, in 60 cc. of carbon tetrachloride was ozonized with ice cooling for two and three-fourths hours. The reaction-mixture was treated with sodium bicarbonate solution and the unchanged precipitate was removed by filtration, and dissolved in acetone. From the decomposition of this precipitate only oxalic acid, identified as the calcium salt, was isolated. Acidification of the alkaline solution gave no solid acid. A gummy, alcohol-insoluble product remained from concentration of the carbon tetrachloride solution at room temperature. Repeated solutions of this residue in alcohol-ether and evaporations *in vacuo* yielded 0.035 g. of dimeric *p*-methoxyphenyl methyl ketone peroxide, which after several recrystallizations from acetone melted at 187.5° with gas evolution.

Anal. Calc'd for $C_{18}H_{20}O_6$: C, 65.05; H, 6.06.
Found: C, 65.25; H, 6.14.

An attempt to isolate *p*-methoxyphenyl methyl ketone from the filtrate as its semicarbazone derivative was unsuccessful. Briner and Nemitz (10) did obtain this derivative in a similar experiment.

Ozonization of dihydroxydibenzal peroxide. A suspension of 0.5 g. of dihydroxydibenzal peroxide in 75 cc. of carbon tetrachloride was ozonized for one and one-half hours and the resulting solution treated with 40 cc. of water for twenty hours. The solvent was removed from the carbon tetrachloride solution *in vacuo* and the residue was dissolved in ether and extracted with dilute aqueous sodium hydroxide. The ethereal solution gave a very small amount of benzaldehyde peroxide, which after recrystallization melted at 195° with gas evolution and red discoloration of the melting point tube, and which showed no depression of melting point with an authentic sample of benzaldehyde peroxide. The alkaline extraction gave 0.3 g. of benzoic acid, melting at 121°.

Treatment of dihydroxydibenzal peroxide with phosphorus pentoxide. Samples of dihydroxydibenzal peroxide in suspension or solution were treated with several grams of phosphorus pentoxide with shaking and cooling, and let stand for various periods of time at low temperature. The solutions were then decanted and the solvents removed *in vacuo*. After testing the residues for explosibility in the flame, the products of the dehydration were fractionally crystallized by treatment with alcohol. The experimental conditions, as well as the quantities of benzaldehyde peroxide isolated, are given in Table III. The characteristic ozonide odor could not be detected in any residue and in no case was a product of explosive character, or of viscous or gelatinous nature, observed. Benzaldehyde and small amount of benzoic acid also were always obtained.

TABLE III

TREATMENT OF DIHYDROXYDIBENZAL PEROXIDE WITH PHOSPHORUS PENTOXIDE

SAMPLE, G.	SOLVENT	TEMPERATURE	TIME, DAYS	YIELD OF BENZALDEHYDE PEROXIDE, G.
0.5	$(C_2H_5)_2O$	Refrigerator (+5°)	2	0.001
2.0	"	"	1	.06 (6.06%)
2.0	"	Acetone-dry ice	2	Trace[a]
3.0	"	Acetone-dry ice	7	0.032[b]
		Ice	$\frac{3}{4}$	
2.0	"	Refrigerator	1	.012[c]
0.5	$CHCl_3$	"	1	.001
2.0	CCl_4	"	2	.061 (6.16%)

[a] After removal of the solvent under a carbon dioxide atmosphere most of the starting material was recovered.

[b] The solvent was removed under a carbon dioxide atmosphere.

[c] Addition of hexane to the concentrated solution produced no precipitate of expected ozonide.

Ozonization of benzaldehyde. A solution of 5 cc. of purified benzaldehyde in 60 cc. of carbon tetrachloride was treated with ozone with ice cooling for one and one-quarter hours. A precipitate, partly crystalline and partly resinous, separated during this time. To the mixture was added 80 cc. of water. After standing overnight, the carbon tetrachloride layer was washed with sodium carbonate. From this alkaline extract 85% of the theoretical amount of benzoic acid was isolated. The carbon tetrachloride solution was evaporated under reduced pressure at room temperature, and the residue was treated with alcohol. A crystalline residue weighing 0.771 g. (15%) of benzoyl peroxide, m.p. 105°, remained. This product showed no depression in melting point when mixed with authentic benzoyl peroxide.

SUMMARY

1. Dimeric diaryl ketone peroxides have been obtained by the ozonolysis of arylated olefins without the introduction of water at any stage of the reaction. This is considered to be evidence in favor of the view that ozonides cleave directly to give the usual products of ozonolysis.

2. Some new dimeric diaryl ketone peroxides and an alkyl aryl ketone peroxide have been characterized.

3. Benzophenone and di-*p*-tolyl ketone have been converted to the corresponding peroxides by the action of hydrogen peroxide.

4. Ozonolyses of styrene, stilbene, and triphenylethylene have yielded dimeric benzaldehyde peroxide.

5. Benzoyl peroxide has been obtained by the ozonization of benzaldehyde.

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