1104 © *1984 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 57,1104—1107(1984)* [Vol. 57, No. 4

Oxidation of *S,S*-Diaryl-*N*-(*p*-tolylsulfonyl)sulfilimines and *N*-Unsubstituted *S,S*-Diaryl-sulfilimines with Potassium Hyperoxide Anion Radical ($O_2^{\overline{\cdot}}$) in the Presence of 1-Bromopropane, Benzoyl Chloride, *p*-Tolylsulfonyl Chloride, Carbon Tetrachloride, Chloroform, or Dichloromethane in Aprotic Media

Kunihiko Akutagawa, Naomichi Furukawa,* and Shigeru Oae*,†
Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun Ibaraki 305

(Received September 2, 1983)

The reaction of *S,S*-diaryl-*N*-(*p*-tolylsulfonyl)sulfilimines and *N*-unsubstituted diaryl-sulfilimines with hyperoxide anion radical ($O_2^{\overline{\cdot}}$) in the presence of 18-crown-6 as a catalyst together with 1-bromopropane/benzene, benzoyl chloride/benzene, *p*-tolylsulfonyl chloride/benzene, carbon tetrachloride, chloroform, or dichloromethane, gave the corresponding sulfoximines, through nucleophilic oxidation with an intermediary dioxy species formed upon treatment of organic halides with potassium hyperoxide (KO_2).

Oxidation is considered to be one of the most important class of reactions which take place on the sulfur atom of organosulfur compounds along with substitution and reduction.[1)] We have been carrying out systematic investigations on the oxidation of organosulfur compounds of various oxidation states,[2)] and suggested that the oxidation which takes place on the sulfur atom is classified mainly into three different types of reactions, based on the electronic demand of the oxidant, *i.e.*, direct one electron transfer oxidation, electrophilic oxidation, and nucleophilic oxidation. The tricoordinate organosulfur species such as sulfoxides[2)] and especially thiosulfinic *S*-esters[2)] are believed to be good models for studying the mechanism of these oxidations and substantial amount of knowledge has been accumulated on the electrophilic and nucleophilic oxidations.[1)] Although sulfilimines are relatively new commers among organosulfur compounds, the chemistry of sulfilimines, isoelectronic species of sulfoxides, has recently been extensively investigated,[3)] the oxidation of sulfilimines is the most effective method to prepare sulfoximines which are widely used as important reagents for organic syntheses such as an alkylidene transfer reagent.[4)] Sodium hypochlorite[5)] and sodium perbenzoate[6)] have been shown to be excellent oxidants to convert the sulfilimines to the corresponding sulfoximines. In many cases, however, many other oxidants, which are used in the oxidation of sulfoxide have been found to react with sulfilimines, affording various undesirable products together with the desired products, sulfoximines, as minor products and sometimes not affording the corresponding sulfoximine at all, or not reacting at all with other oxidants, recovering the original sulfilimines.[7)] In general, electrophilic oxidation of sulfilimines fails to afford the corresponding sulfoximines, while nucleophilic one is expected to oxidize sulfilimines successfully to the corresponding sulfoximines.

Hyperoxide anion radical ($O_2^{\overline{\cdot}}$) is known to be an effective nucleophile in aprotic solvents.[8)] Alkyl halide is known to react with hyperoxide anion radical through an S_N2 mechanistic path and yields the alkyl peroxide as an overall product *via* formation of alkylperoxyl radical and alkyldioxy anion[9)] in the initial step. The *p*-tolylsulfonyl chloride–potassium hyperoxide reaction yields an intermediate *i.e.*, *p*-tolylsulfonylperoxoate anion which oxidized sulfoxides, phosphines, or electrophilic olefins to afford the corresponding sulfones, phosphine oxides or epoxides.[2)] Although *S,S*-diaryl-*N*-(*p*-tolylsulfonyl)-sulfilimines have not been oxidized readily with various oxidizing systems, many of these oxidizing systems are electrophilic oxidants. According to a concept of electrophilic and nucleophilic oxidations,[10)] *N*-(*p*-tolylsulfonyl)sulfilimines are liable to be attacked by nucleophilic oxidants, since the central sulfur atom is tricoordinate and hence the electron density around the central sulfinimidoyl sulfur atom is decreased. Meanwhile, since the following dioxy species, *i.e.*, alkyldioxy species (ROO^-), acyldioxy species ($AcOO^-$), or sulfonyldioxy species($TsOO^-$), generated *in situ* in the treatment of alkyl halide, acyl halide, or tosyl chloride with hyperoxide anion radical, are believed to be markedly more nucleophilic oxidizing agents than hyperoxide anion radical alone, even *S,S*-diaryl-*N*-(*p*-tolylsulfonyl)sulfilimines, which are inert to hyperoxide anion radical alone, are expected to be selectively oxidized with the reactive dioxy intermediates to afford the corresponding sulfoximines successfully, as in the nucleophilic oxidation of *S,S*-diaryl-*N*-(*p*-tolylsulfonyl)sulfilimine with such a powerful nucleophilic oxidant as hypochlorite anion.[5b)]

This paper describes the successful oxidations of sulfilimines with hyperoxide anion radical in a few reaction systems.

Results and Discussion

S,S-*Diaryl*-N-(p-*tolylsulfonyl)sulfilimine.* Hyperoxide anion radical was generated *in situ* by mixing potassium hyperoxide and 18-crown-6 as a catalyst in an apropriate solvent such as benzene under argon atmosphere. At first,when *S,S*-diphenyl-*N*-(*p*-tolylsulfonyl)sulfilimine was treated with hyperoxide anion radical in the presence of 18-crown-6 as catalyst in benzene without any additive, such as an organic halide, there was no formation of any oxidized pro-

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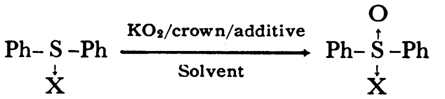
† Present adress; Okayama University of Sciences, Ridaicho, Okayama 700.

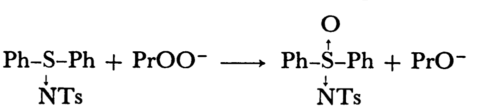
duct, *i.e.*, the corresponding sulfoximine, and the sulfilimine was recovered quantitatively after 24 h. A few additives were examined which are capable of generating more effective dioxy species to convert *S,S*-diphenyl-*N*-(*p*-tolylsulfonyl)sulfilimine to the corresponding sulfoximine selectively. Addition to such an alkyl halide, as 1-bromopropane to the above reaction system in the presence of 18-crown-6 or "dicyclohexyl-18-crown-6" was found to give the corresponding sulfoximine in 91% or 94% yields respectively. Diphenyl sulfoxide, an isoelctromer of the sulfilimine, was also oxidized to diphenyl sulfone in this reaction system. Other additives, such as benzoyl chloride and *p*-tolylsulfonyl chloride, were also found to be effective in the oxidation of *S,S*-diphenyl-*N*-(*p*-tolylsulfonyl)sulfilimine to the sulfoximine under mild conditions. The results are summarized in the following equation 1.



$$\underset{\overset{\downarrow}{X}}{\text{Ph-S-Ph}} \xrightarrow[\text{Solvent}]{\text{KO}_2\text{/crown/additive}} \overset{O}{\underset{\overset{\downarrow}{X}}{\text{Ph-}\overset{\uparrow}{\text{S}}\text{-Ph}}} \qquad (1)$$

X: $NSO_2C_6H_4CH_3$-*p*, O, NH.
Crown: 18-crown-6, "dicyclohexyl-18-crown-6".
Additive: 1-bromopropane, PhCOCl, TsCl, CH_2Cl_2, $CHCl_3$, CCl_4.
Solvent: benzene.

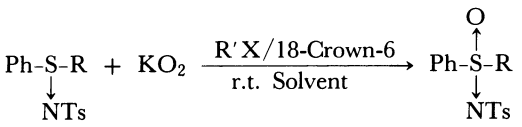
This oxidation, however, did not proceed at all without the crown ether. Thus, the sulfilimine is considered to be oxidized by the intermediary reactive dioxy anion species, incipiently formed *in situ* in the treatment of these organic halides with hyperoxide anion radical in the presence of the crown ether (Eq. 2).



$$\text{PrBr} + O_2^- \longrightarrow \text{PrOO}^-$$
$$\text{PrOO}^- + O_2^- \longrightarrow \text{PrOO}^- + O_2$$
$$\underset{\overset{\downarrow}{\text{NTs}}}{\text{Ph-S-Ph}} + \text{PrOO}^- \longrightarrow \overset{O}{\underset{\overset{\downarrow}{\text{NTs}}}{\text{Ph-}\overset{\uparrow}{\text{S}}\text{-Ph}}} + \text{PrO}^- \qquad (2)$$

Several other sulfilimines were also converted to the corresponding sulfoximines in good yields. Halogenated solvents such as dichloromethane, chloroform, or carbon tetrachloride[11] were also found to assist the oxidation of this type. These results were summarized in Table 1. *S*-(*p*-Nitrophenyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimine was found to afford unidentified products. No original sulfilimine was recovered.** *S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)-sulfilimine was not oxidized at all in this system. The original sulfilimine was recovered though the isoelectronic methyl phenyl sulfoxide was readily oxidized to the corresponding sulfone in 78% yield.

Table 1. Oxidation of *N*-tosylsulfilimines

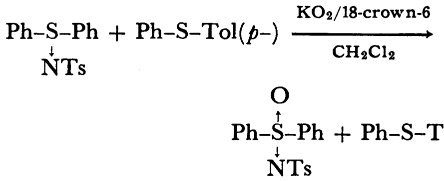


$$\underset{\overset{\downarrow}{\text{NTs}}}{\text{Ph-S-R}} + \text{KO}_2 \xrightarrow[\text{r.t. Solvent}]{\text{R}'\text{X/18-Crown-6}} \overset{O}{\underset{\overset{\downarrow}{\text{NTs}}}{\text{Ph-}\overset{\uparrow}{\text{S}}\text{-R}}}$$

R	Time/h	Solvent	R′X	Yield/%[a]
Ph	3	Benzene	PrBr	91
Ph	24	Benzene	None	0
Ph	2	Benzene	*p*-TsCl	94
Ph	3	Benzene	PhCOCl	86
Ph	2	CH_2Cl_2		97
Ph	2	$CHCl_3$		92
Ph	2	CCl_4		90
p-Tol	2	CH_2Cl_2		87
p-ClC_6H_4	2	CH_2Cl_2		91
p-$NO_2C_6H_4$	10	CH_2Cl_2		0
Me	24	CH_2Cl_2		Trace

a) Isolated yield.

In this reaction, the relatively acidic α-hydrogen atom of this sulfilimine may be immediately deprotonated by hyperoxide anion radical, or peroxyl radical to stop the reaction, because of the formation of the hydroperoxy species (HOO^-) which are incapable of nucleophilic oxidation. Incidentally, acetonitrile was found to react with disulfide in the presence of hyperoxide anion radical to form bis(arylthio)acetonitrile.[2,13] Initial formation of cyanomethyl radical has been proposed for this reaction. The formation of peroxide ion (O_2^{2-}), which may exist in this reaction system by disproportionation of hyperoxide anion (O_2^-) can be ruled out, since the reaction of *S,S*-diphenyl-*N*-(p-tolylsulfonyl)sulfilimine with Na_2O_2 in the presence of 18-crown-6 in benzene under argon atmosphere resulted in the partial reduction of this sulfilimine to give diphenyl sulfide in 30% yield together with the recovered sulfilimine in 70% after 24 h. Dimethyl sulfide and methyl phenyl sulfide were found not to be oxidized at all under these conditions. Thus, treatment of a mixture of *S,S*-diphenyl-*N*-(*p*-tolylsulfonyl)sulfilimine and phenyl *p*-tolyl sulfide with potassium hyperoxide in dichloromethane at 25 °C for 2 h in the presence of catalytic amount of 18-crown-6 in argon atmosphere gave *S,S*-diphenyl-*N*-(*p*-tolylsulfonyl)sulfoximine quantitatively, recovering the added phenyl *p*-tolyl sulfide quantitatively, but not phenyl *p*-tolyl sulfoxide or sulfone (Eq. 3).



$$\underset{\overset{\downarrow}{\text{NTs}}}{\text{Ph-S-Ph}} + \text{Ph-S-Tol}(p\text{-}) \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{KO}_2\text{/18-crown-6}} \overset{O}{\underset{\overset{\downarrow}{\text{NTs}}}{\text{Ph-}\overset{\uparrow}{\text{S}}\text{-Ph}}} + \text{Ph-S-Tol}(p\text{-}) \qquad (3)$$

Phenyl *p*-tolyl sulfide was not oxidized at all even after prolonged reaction time, 24 h, with this nucleophilic oxidation system. These results strongly support that

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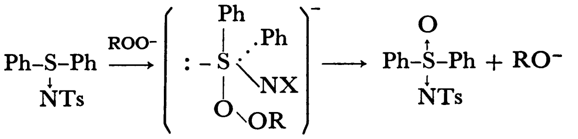
** Upon addition of this sulfilimine into the solution of hyperoxide anion in benzene in the presence of 18-crown-6 without any additive, *e.g.*, 1-bromopropane, one finds rapid color change (from colorless heterogeneous solution into dark bluish solution) of the solution, which eventually gave unidentified products, without recovering the starting material. Perhaps, an S_{RN} type substitution reaction[12] of hyperoxide anion radical with this sulfilimine, which is activated by nitro group, would have taken place involving one electron transfer from hyperoxide anion into the sulfilimine, followed by subsequent reaction of the aromatic anion radical with oxygen or hyperoxide anion radical, or subsequent breaking down to give unidentified products.

the reactive dioxy anion species (ROO$^-$) was initially formed and then oxidized *S*,*S*-diphenyl-*N*-(*p*-tolylsulfonyl)sulfilimine, but not the sulfide. The hydroperoxide (ROOH) intermediate may not be formed during the reaction, since it would readily oxidize the sulfide but not the sulfilimine in this system. Although there is no legitimate evidence to clarify the mechanism for this oxidation by ROO$^-$, we propose that this oxidation may involve the initial formation of unstable sulfurane intermediate by the nucleophilic attack of dioxy anion toward the electrophilic center of sulfinimidoyl sulfur atom of the sulfilimine which readily breaks down to the corresponding sulfoximine and alkoxide anion in the subsequent step as shown in Eq. 4. This sulfurane intermediate has been proposed in the nucleophilic oxidation of sulfoxides or sulfilimines with hypochlorite anion.[2,5b)] Nor was there any good correlation between the effect of substituent and the yield of the sulfoximine as depicted in Table 1, unlike those of the nucleophilic oxidation of sulfoxides by perbenzoic acid[14)] or alkyldioxy anion[14)] or of *N*-(arylsulfonyl)sulfilimine by hypochlorite anion[5b)] in which fairly good Hammett correlations have been found to hold. A similar phenomenon was observed in the oxidation of sulfoxide with hyperoxide anion radical in the presence of di-*p*-tolyl disulfide,[2)] or in the S_N2 type substitution reaction of primary or secondary alkyl halide with hyperoxide anion radical.[9,15)]



$$\underset{\downarrow\atop \mathrm{NTs}}{\mathrm{Ph\text{-}S\text{-}Ph}} \xrightarrow{\mathrm{ROO^-}} \left(:\text{-}\mathrm{S}\overset{\mathrm{Ph}}{} \begin{smallmatrix}\mathrm{.Ph}\\ \mathrm{NX}\end{smallmatrix} \underset{\mathrm{O\diagdown OR}}{} \right)^- \longrightarrow \underset{\downarrow\atop \mathrm{NTs}}{\mathrm{Ph\text{-}\overset{O\atop\uparrow}{S}\text{-}Ph}} + \mathrm{RO^-} \qquad (4)$$

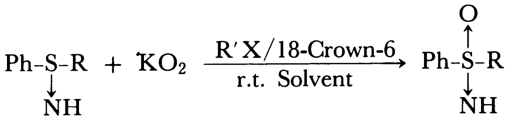
Similar dioxy anion species have been postulated in the epoxidation of electrophilic olefins or in the oxidation of sulfoxides to the corresponding sulfones.[16,17)] Gibian and Ungermann found that dimethyl sulfoxide used as solvent was oxidized during the reaction of alkyl halide with hyperoxide anion radical by the intermediary active oxidizing species, an alkyldioxy anion.[15)]

Thus, in the presence of organic halides and a catalytic amount of the crown ether, potassium hyperoxide was found to oxidize *S*,*S*-diaryl-*N*-(*p*-tolylsulfonyl)sulfilimines which have no nitro group to the corresponding sulfoximines.

N-Unsubstituted S,S-Diarylsulfilimine. *N*-Unsubstituted diarylsulfilimines were reported to be oxidized selectively to the corresponding sulfoximines by sodium hypochlorite,[5a)] potassium permanganate,[7a)] and sodium periodate.[16)] No good result was obtained by oxidation with *m*-chloroperbenzoic acid,[7a)] and hydrogen peroxide in acidic media such as acetic acid[7a)] or in neutral media.

In the absence of alkyl halide, unsubstituted diphenylsulfilimine did not react with potassium hyperoxide in the presence of 18-crown-6 in benzene only to afford the recovered sulfilimine even after 24 h. However, the same oxidation in the presence of 1-bromopropane proceeded successfully giving the corresponding sulfoximine in 75% yield. The sulfilimine was also oxidized in dichloromethane which functions both as solvent and reactant, affording the corresponding sulfoximine in a good yield. These results are listed in Table 2. *S*-(*p*-Nitrophenyl)-*S*-phenylsulfilimine reacted with potassium hyperoxide in the absence of alkyl halide to afford various unidentified products, but not afford the corresponding sulfoximine. The oxidation of the unsubstituted sulfilimine is considered to proceed similarly as in the case of *S*,*S*-diphenyl-*N*-(*p*-tolylsulfonyl)sulfilimine, namely *via* involving sulfurane as an intermediate as shown in equation 4.

TABLE 2. OXIDATION OF *N*-UNSUBSTITUTED SULFILIMINES



$$\underset{\downarrow\atop \mathrm{NH}}{\mathrm{Ph\text{-}S\text{-}R}} + \mathrm{KO_2} \xrightarrow[\mathrm{r.t.\ Solvent}]{\mathrm{R'X/18\text{-}Crown\text{-}6}} \underset{\downarrow\atop \mathrm{NH}}{\mathrm{Ph\text{-}\overset{O\atop\uparrow}{S}\text{-}R}}$$

R	Time/h	Solvent	R'X	Yield/%[a)]
Ph	3	Benzene	PrBr	75
Ph	24	Benzene	None	0
Ph	1	CH_2Cl_2		84
p-Tol	1	CH_2Cl_2		89
p-$NO_2C_6H_4$	10	CH_2Cl_2		0

a) Isolated yield.

All these reactions reveal clearly that tricoordinate organosulfur compounds are oxidized to the corresponding tetracoordinate sulfur compounds much more effectively by nucleophilic oxidants as we have anticipated.

In summary, *S*,*S*-diaryl-*N*-(*p*-tolylsulfonyl)sulfilimines and unsubstituted diarylsulfilimines were selectively oxidized to the corresponding sulfoximines upon treatment with potassium hyperoxide in the presence of organic halides.

Experimental

General. Melting points of the products were measured by Yanaco instrument and were uncorrected. IR spectra were obtained using a Hitachi 215 spectrophotometer. ^{1}H NMR spectra of all the compounds were obtained with a Hitachi Perkin-Elmer R-20 spectrometer in 20% deuteriochloroform solution using tetramethylsilane as an internal standard. Liquid chromatographs were obtained by Yanaco-L-1030 instrument using methanol as an eluent. Thin layer chromatographs were carried out with Merck DC-Plastikofolien Kieselgel 60 F 254 Art 5735 with fluorescent indicator using various solvents and mixed solvents. Development was followed with UV light or by coloring with iodine. Silica gel used for column chromatography was either of Wako or Merck chromatographic grade. Elemental analyses were carried out by the Chemical Center of this University. Potassium hyperoxide was obtained from Veutron Alfa Products. 18-Crown-6 and "dicyclohexyl-18-crown" were obtained from Wako Pure Chemicals and used after drying *in vacuo* at 60—70 °C. Anhydrous dichloromethane, chloroform, and carbon tetrachloride were obtained by distillation of first grade commercial products and then dried over calcium dichloride just before use. Benzene was purified by distillation similarly and dried over metal sodium under nitrogen. *p*-Tolylsulfonyl chloride from Wako Pure Chemicals were used after recrystallization from hexane.

Benzoyl chloride was purified by distillation after dehydration with calcium dichloride. Extra pure reagent 1-bromopropane from Wako Pure Chemicals was used directly without any further treatment. Other chemicals were of reagent grade.

Materials. *N*-(*p*-Toylylsulfonyl)sulfilimines *i.e.*, *S,S*-dimethyl-, *S*-methyl-*S*-phenyl-. *S,S*-diphenyl-, *S*-(*p*-tolyl)-*S*-phenyl-, *S*-(*p*-chlorophenyl)-*S*-phenyl-, *S*-(*p*-nitrophenyl)-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfilimines were prepared by treatment of the corresponding sulfides with chloramine-T in methanol, according to the method reported earlier.[19] *N*-Unsubstituted sulfilimines *i.e.*, *S,S*-diphenyl-, *S*-phenyl- *S*-(*p*-tolyl)-, *S*-(p-nitrophenyl)-*S*-phenylsulfilimines were prepared by treatment of the corresponding *N*-(*p*-tolylsulfonyl)sulfilimines with concentrated sulfuric acid and then with aqueous sodium hydroxide solution according to a known method.[7a)]

Reaction of S,S-*Diphenyl*-N-(p-*tolylsulfonyl)sulfilimine with Potassium Hyperoxide in Benzene in the Presence of 1-Bromopropane and Catalytic Amount of 18-Crown-6.* To a finely powdered potassium hyperoxide (252 mg, 3.5 mmol) was injected a solution of the title sulfilimine (501 mg, 1.4 mmol) and 18-crown-6 (0.08 mmol) in dry benzene and then a solution of 1-bromopropane (260 mg, 2.1 mmol) in the same solvent was added into a two-necked flask under dry argon atmosphere at room temperature. The resulting heterogeneous mixture stirred at the same temperature for 3 h. The reaction was monitored by TLC or HPLC until the substrate disappeared nearly completely. After the reaction, the reaction mixture was poured into a large excess of ice-water, extracted with chloroform, washed with water, and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the crude corresponding sulfoximine was obtained. Purification was accomplished by column chromatography through silica gel using chloroform as an eluent. The corresponding sulfoximine was obtained in 91% yield. In the reactions in which *p*-tolylsulfonyl chloride and benzoyl chloride were used as organic halides, the above mentioned procedure was also applied.

Oxidation of S,S-*Diphenyl*-N-(p-*tolylsulfonyl)sulfilimine with Potassium Hyperoxide in Dichloromethane in the Presence of 18-Crown-6.* A solution of the title sulfilimine (500 mg, 1.4 mmol) in dry dichloromethane was added to a finely powdered potassium hyperoxide (252 mg, 3.5 mmol) and dry 18- crown-6 (0.07 mmol) in a two-necked flask under dry argon atmosphere at room temperature. The mixture was stirred at the same temperature for 2 h, monitoring by HPLC. After the consumption of the substrate, the work-up described before was carried out. The corresponding sulfoximine was obtained in 97% yield.

Oxidation of N-*Unsubstituted Diphenylsulfilimine with Potassium Hyperoxide in Dichloromethane in the Presence of 18-Crown-6.* To a finely powdered potassium hyperoxide (440 mg, 6.2 mmol) was added a solution of the title sulfilimine (500 mg, 2.5 mmol) and dry 18-crown-6 in dry dichloromethane in a two-necked flask under dry argon atmosphere at room temperature. The heterogeneous solution was stirred at the same temperature for 1 h. After the starting sulfilimine was found to have disappeared, upon monitoring by TLC or HPLC, the reaction mixture was poured into excess water. After the usual work-up and separation by column chromatography, diphenyl sulfide (6%) and diphenylsulfoximine (84%) were obtained.

We express our thanks to Dr.Toshikazu Takata for his collaboration.

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