Photoinduced Electron Transfer Reactions of Aryl Benzyl Sulfides Promoted by 2,4,6-Triphenylpyrilium Tetrafluoroborate (TP⁺BF₄⁻)

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Received August 1, 2005

Photocatalytic electron transfer reactions of aryl benzyl sulfides using 2,4,6-triphenylpyrilium tetrafluoroborate (TP⁺BF₄⁻) resulted in the oxidation of these sulfides to the corresponding sulfoxides and also in most cases in the C-S bond cleavage of them along with formation of aromatic aldehydes. In these reactions, the formation of sulfide radical cation has been proposed, which undergoes either oxidation to the corresponding sulfoxide or C-S bond cleavage to the formation of aromatic aldehydes. The further oxidation of sulfoxides to sulfones has not been observed. The influence of substrate structures on the reaction pathways as well as the role of O_2 in this respect is discussed.

Key Words : Electron transfer, Aryl benzyl sulfides, Sulfoxides, Photocleavage, Photochemistry

Introduction

Photooxidation of organic sulfides has been extensively studied and is still under investigation. This reaction has received extensive study under a variety of reaction conditions, namely, I) autooxidation,[1-4] II) electron transfer sensitization[5-12] and III) singlet oxygen oxidation.[13-22] A mechanism involving radical cation intermediates of sulfides was proposed for the electron transfer sensitized reactions using titanium dioxide[6,8] 2,4,6-tri(*p*-chlorophenyl)pyrilium perchlorate (TCPPClO₄),[7] 9,10-dicyanoanthracene[7,9-12] and *N*-methylquinolinium tetrafluoroborate,[12] but none of these works has reported the results of the photoreaction of various organic sulfides to elucidate the type of the aryl group on the extent of C-S bond cleavage *vs.* S-oxidation like our present work.

Photoinduced electron transfer (PET) processes have attracted growing interest in the last decade and many reactions such as cycloadditions, cycloreversions, oxygenations and fragmentations have been documented.[23-28]

2,4,6-Triphenylpyrylium tetrafluoroborate (TP⁺BF₄⁻) absorbs in the visible region and is a strong oxidizing agent in the excited state. The advantage of the use of this compound as a PET-sensitizer is its high solubility in many organic solvents and due to its salty character (TP⁺BF₄⁻), no net charge separation is needed for the electron transfer step, since pyrilium ring accept the electron, which is already separated from its counter ion, namely BF₄⁻. This leads to enhancement of the formation of free radical cation from donor molecule because of reduced back electron transfer. The result is an increase of the efficiency of quantum yield of PET-reactions.

Recently, we have reported on photoinduced electron transfer ring opening of *α*-epoxyketones using 2,4,6-triphenylpyrilium tetrafluoroborate (TP⁺BF₄⁻) as photocatalyst in methanol,[29] acetone,[30] cyclohexanone[31] and acetic acid solutions.[32] We found out that TP⁺BF₄⁻ is a powerful photoelectron acceptor compared with TiO_2[33] and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ).[34]

Now we wish to introduce the results of our investigation on the photoinduced oxidation of aryl benzyl sulfides with TP⁺BF₄⁻.

Results and Discussion

In a typical reaction, an oxygenated solution of sulfide (1 mmol) and TP⁺BF₄⁻ (0.05 mmol) in acetonitrile was irradiated for the time given in Table 1. The progress of the reaction was followed by TLC and irradiation has been continued until total disappearance of the sulfides (Scheme 1). The results are summarized in Table 1.

Regarding to result from the control experiments and the results presented in Table 1 we found out that:

1. The presence of photocatalyst TP⁺BF₄⁻ is necessary for the reaction, because irradiation of **1a** without TP⁺BF₄⁻ as a test experiment does not result in the occurrence of any reactions.

2. The formation of the observed products by direct excitation of sulfides is ruled out, since the light has been passed through a filter solution to cut-off the UV light which might be absorbed by the sulfides.

3. The presence of oxygen is necessary for the reaction, since no products have been observed to be generated on irradiation of **1a** and TP⁺BF₄⁻ under argon atmosphere.

4. Two types of reactions, oxidation of sulfides to the corresponding sulfoxides and C-S bond cleavage and consequently formation of arylaldehydes have been observed.

On the basis of the foregoing results, the following mechanism is proposed for the reaction (Scheme 2):

According to the proposed mechanism, a photoinduced electron transfer from sulfide to the excited photocatalyst TP⁺BF₄⁻ leads to the formation of sulfide radical cation **6**. In the case of benzyl sulfides **1a-1k**, deprotonation of **6** and formation of *α*-thiophenoxy carbon radical **7** is the

Scheme 1
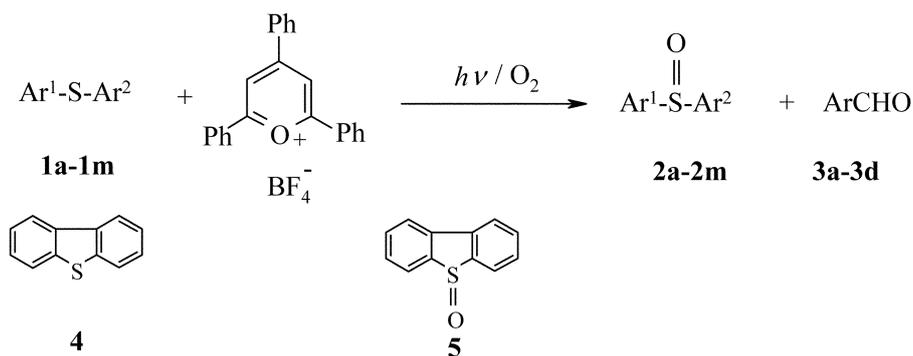
Table 1. Products of photoelectron transfer reactions of sulfides by $TP^+BF_4^{-\ I}$

Comp.	Ar^1	Ar^2	Product (%Yield)[III,IV]		T/min^V
			Sulfoxide	Aldehyde/Ar	
1a	C_6H_5	$C_6H_5CH_2$	**2a** (14)	**3a**, C_6H_5 (38)	120
1b	C_6H_5	$p\text{-}BrC_6H_4CH_2$	**2b** (15)	**3b**, $p\text{-}BrC_6H_4$ (40)	60
1c	C_6H_5	$p\text{-}CH_3C_6H_4CH_2$	**2c** (3)	**3c**, $p\text{-}CH_3C_6H_4$ (43)	40
1d	C_6H_5	$p\text{-}NO_2C_6H_4CH_2$	**2d** (3)	**3d**, $p\text{-}NO_2C_6H_4$ (46)	50
1e	$p\text{-}CH_3C_6H_4$	$C_6H_5CH_2$	**2e** (15)	**3a**, C_6H_5 (40)	60
1f	$p\text{-}CH_3C_6H_4$	$p\text{-}BrC_6H_4CH_2$	**2f** (15)	**3b**, $p\text{-}BrC_6H_4$ (41)	65
1g	$p\text{-}ClC_6H_4$	$C_6H_5CH_2$	**2g** (16)	**3a**, C_6H_5 (38)	70
1h	$p\text{-}ClC_6H_4$	$p\text{-}BrC_6H_4CH_2$	**2h** (16)	**3b**, $p\text{-}BrC_6H_4$ (39)	70
1i	$p\text{-}ClC_6H_4$	$p\text{-}NO_2C_6H_4CH_2$	**2i** (6)	**3d**, $p\text{-}NO_2C_6H_4$ (44)	55
1j	$C_6H_5CH_2$	$p\text{-}BrC_6H_4CH_2$	**2j** (14)	**3a**, C_6H_5 (10) **3b**, $p\text{-}BrC_6H_4$ (30)	150
1k	$C_6H_5CH_2$	$C_6H_5CH_2$	**2k** (15)	**3a**, C_6H_5 (37)	170
1l	C_6H_5	C_6H_5	**2l** (93)		300
1m	2-pyridyl	$2,4\text{-}(NO_2)_2C_6H_3$	**2m** (0)		300
4			**5** (95)		300

[I][**1a-m,4**] : [$TP^+BF_4^-$] = 20 : 1, [II]Isolated yields. [III]The aldehydes obtained in the reaction have been characterized with the physical and spectral data with those of authentic samples. [IV]In the case of **1a-1k**, arylsulfonic acids could not be isolated by chromatography methods, therefore, the yield of these acids has not been determined. [V]The times are given for total conversion of the sulfides.

Scheme 2
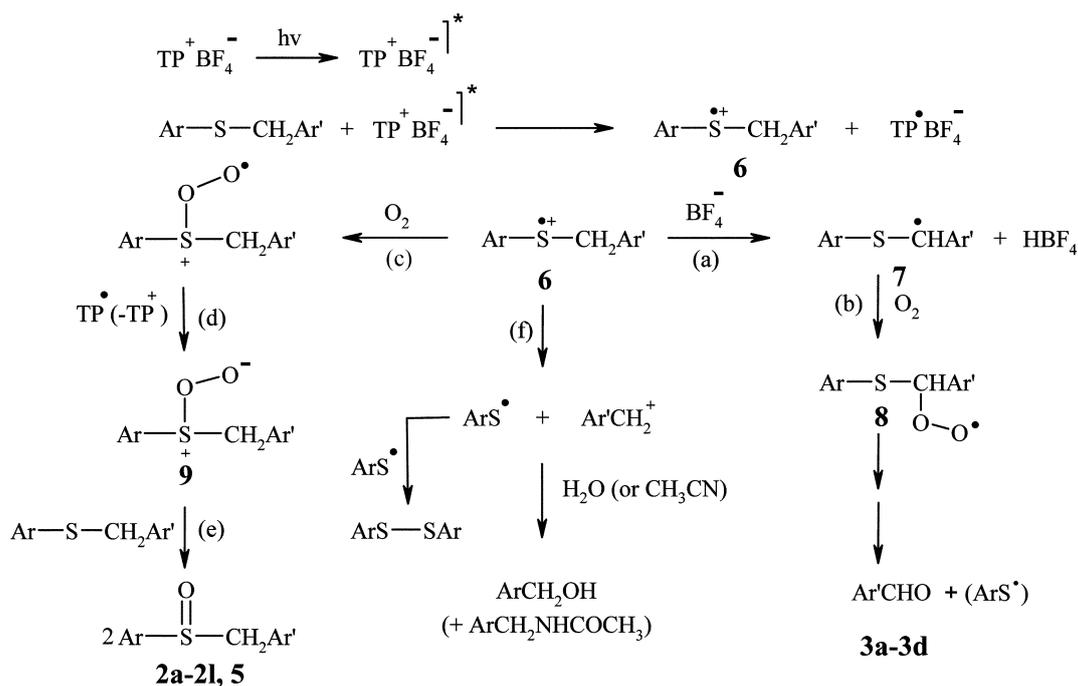
predominant path for the radical cation intermediate **6** and therefore arylaldehydes **3a-3d** are formed as the major products accompanied by less amounts of sulfoxides **2a-2k**. In this reaction the intermediate **7** should react with O_2 to give a peroxy radical **8** whose conversion to arylaldehydes **3a-3d** has been shown. This suggestion is supported by the formation of the aldehydes, namely, benzaldehyde **3a** and 4-bromobenzaldehyde **3b** from unsymmetrical benzylic sulfide **1j** through the paths.

Oxidative cleavage of carbon-sulfur bond during reactions of alkyl benzyl sulfides with singlet oxygen using Tetraphenylporphyrin-Zn complex as sensitizer was first reported by Corey *et al.* in 1976.[35] Besides products deriving from C-S bond cleavage, the formation of the corresponding sulfoxides and sulfones have also been observed during these reactions. According to the proposed mechanism for the C-S bond cleavage, the attack of singlet oxygen to sulfides leads to the formation of radical or ionic intermediate, which undergoes Pummerer rearrangement to the observed products, namely, sulfoxides, sulfones and aldehydes.[36] Since $TP^+BF_4^-$ is not able to participate in energy transfer from its excited state to ground state oxygen,[37,38] therefore, the involvement of singlet oxygen in our reaction for the C-S bond cleavage is ruled out. As we expected, oxidative cleavage of carbon-sulfur bond from sulfide radical cation intermediate **6** in our reactions can be observed only in the case of sulfides **1a-1k** with benzylic substituent. It should be noted that in this case, we have isolated the corresponding aldehyde **3a-3d** as major product and we did not find any product derived from thienyl radical (RS•) intermediate such as arylsulfinic and arylsulfonic acids. As it has been reported these acids should be normally formed from the O_2 promoted oxidation of the sulfur containing species produced in the C-S bond cleavage pathway (arylthyil radical and its dimerization products).[39,40] The formation of these compounds have been reported on reaction of organic sulfur compounds with superoxide anion.[40] The formation of benzenesulfonic acid by photoinduced electron transfer reactions of benzyl phenyl sulfides promoted by 9,10-dicyanoanthracene has been reported, but the yield is not determined.[9] It should be noted that decreased yields of the observed products in the cases of sulfides **1a-1k** is due to arylsulfonic acid, which could not be isolated by the chromatography methods, and therefore, their yields are not able to be measured and listed in the Table 1.

The sulfoxide products are probably formed by reaction of radical cation intermediate **6** with O_2, leading to the formation of a persulfoxide intermediate **9** that is presumably able to oxidize another sulfide molecule to sulfoxide. This reaction through the paths c, d and e occurs exclusively in the cases of sulfides **1l** and **4**, since they do not have an α-hydrogen containing benzylic substituent and the C-S bond cleavage is not expected.

An interesting result in our reaction is the influence of substrate structure on the reaction pathways. Whereas diphenyl sulfide **1l**, 2,4-dinitrophenyl 2-pyridyl sulfide **1m** and also dibenzothiophene **4** which do not have benzylic

methylene group did not give the products derived from C-S bond cleavage, because of unstability of radical cation **6** with electron-withdrawing group ($-NO_2$) oxidation of **1m** to the corresponding sulfoxide **2m** did not observe even after irradiation for 5h. And, path f does not occur in **1a-k**. The effect of various substituents on the phenyl group of the benzyl moiety, bromine **1b**, methyl **1c**, and nitro groups **1d** instead of hydrogen **1a**, is not clear since the irradiation time for completion of reaction and also the yield of photocleavage is not varied too much from each other, but their presence compared with hydrogen decrease the irradiation time

The involvement of superoxide anion, O_2^-, in the reaction with sulfide radical cation for the formation of sulfoxide has been reported using 9,10-dicyanoanthracene[9,14] or titanium dioxide.[6] In the case of $TP^+BF_4^-$, which we used as photocatalyst in our reactions, formation of superoxide anion, O_2^-, is not possible since cyclic voltammetry studies of dicyanoanthracene and $TP^+BF_4^-$ indicate that in contrast to dicyanoanthracene radical anion, triphenylpyryl radical TP is not able to transfer an electron to molecular oxygen under formation of superoxide anion O_2^- and triphenylpyryl cation TP^+.[37,38,41]

Finally, a noteworthy result in our reaction is that the possibility of further oxidation of initially formed sulfoxides to sulfones is ruled out, since we did not observe any trace of any sulfones even with the TLC of the authentic sulfones although sulfones are easily detected and isolated by chromatography methods. However the formation of sulfones by the photosensitized oxidation of sulfoxides has been reported using dicyanoanthracene and rose Bengal.[10,14]

The advantage of this catalyst is the use of lower molar ratio of catalyst:sulfide (1 : 20) in our reactions compared with dicyanoanthracene : sulfide (1 : 10)[9] and dimethoxynaphthalene : sulfide (1 : 2)[17] in photoinduced electron transfer reaction of sulfides and also the observed photocleavage of C-S bond. It should be noted that overoxidation of sulfoxides to corresponding sulfones has not been observed, whereas overoxidation of dibenzothiophene **4** to dibenzothiophene sulfone has been reported using dicyanoanthracene.[10] Other sulfides, diphenyl sulfide **1l** and dibenzothiophene **4** have been converted efficiently to the corresponding sulfoxides after irradiation for 5 h, whereas Baciocchi et al have obtained only 10% of diphenyl sulfoxide **2l** on irradiation of diphenyl sulfide **1l** by using TiO_2 in CH_3CN in the presence of Ag_2SO_4 after irradiation for 4 h.[8] It should also be noted that no reactions of the aryl benzyl sulfides has been observed using 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) as a photocatalyst.

Conclusion

In conclusion, this work describes electron transfer induced photooxidation reaction of aryl benzyl sulfides to the corresponding sulfoxides and to the aromatic aldehydes through C-S bond cleavage.

Experimental Section

Melting points were determined on a Stuart Scientific SMP2 apparatus and are uncorrected. IR spectra were recorded on a Shimadzu apparatus IR 435. ^{1}H NMR spectra were recorded on Bruker 200 and 500 MHz. Elemental analyses were carried out on CHNO-rapid Heraeus. Starting materials have been prepared according to the known procedures[42,43] and also by adoption of them for the new compounds. Preparative layer chromatography (PLC) was carried out on 20 × 20 cm^2 plates, coated with 1mm layer of Merck silica gel PF$_{254}$, prepared by applying the silica as a slurry and drying in air.

All irradiations were carried out in a 25 mL pyrex cell using a 400 W high pressure Hg vapor lamp from NARVA and cooling of sample by running water. The light has been passed through a filter solution containing 75 g·L^{-1} of NaNO$_2$ and 4.4 g·L^{-1} of CuSO$_4$ in 2.7 M NH$_4$OH to obtain λ ≥ 400 nm for the selective excitation of the photocatalyst TP$^+$BF$_4^-$ and also to prevent the absorption of the light by the sulfides **1a-m** and **4**.

General procedure for the irradiation of sulfides in the presence of TP$^+$BF$_4^-$. A solution of 1 mmol of sulfides and 0.05 mmol of 2,4,6-triphenylpyrilium tetrafluoroborate (TP$^+$BF$_4^-$) in 20 mL oxygenated acetonitrile was irradiated for the time given in Table 1 until total disappearance of sulfides had been observed. After completion of the reaction, solvent was evaporated under reduced pressure and the products were isolated by PLC using n-hexane/ethyl acetate (7 : 2, v/v) as eluent.

Physical and spectral data of sulfoxides are as follows:

Benzyl phenyl sulfoxide 2a: m.p. 122-123 °C, m.p.[44] 122-124 °C. IR (KBr): 1034 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): 4.04 (d, 1 H, J = 12.6 Hz), 4.14 (d, 1 H, J = 12.6 Hz), 7.02-7.03 (m, 2 H), 7.28-7.36 (m, 3 H), 7.41-7.52 ppm (m, 5 H).

4-Bromobenzyl phenyl sulfoxide 2b: m.p. 178-179 °C, m.p.[45] 179 °C. IR (KBr): 1029 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): 3.98 (d, 1 H, J = 12.8 Hz), 4.05 (d, 1 H, J = 12.8 Hz), 6.86 (d, 2 H, J = 8.3 Hz), 7.31-7.51 ppm (m, 7 H).

4-Methylbenzyl Phenyl Sulfoxide 2c: m.p: 97-99 °C, m.p.[46] 99-100 °C. IR (KBr): 1027 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): 2.36 (s, 3 H), 3.99 (d, 1 H, J = 12.6 Hz), 4.10 (d, 1 H, J = 12.6 Hz), 6.91 (d, 2 H, J = 7.70 Hz), 7.10 (d, 2 H, J = 7.70 Hz), 7.42-7.51 (m, 5 H).

4-Nitrobenzyl Phenyl Sulfoxide 2d: m.p: 161-163 °C. IR (KBr): 1026, 1345, 1515 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): 4.04 (d, 1 H, J = 12.0 Hz), 4.24 (d, 1 H, J = 12.0 Hz), 7.13 (d, 2 H, J = 6.5 Hz), 7.40-7.51 (m, 5 H), 8.12 (d, 2 H, J = 6.5 Hz). Analysis Calcd. for C$_{13}$H$_{11}$NSO$_3$: C, 59.76; H, 4.24; N, 5.36; S, 12.27. Found: C, 59.3; H, 4.4; N, 5.1.

Benzyl 4-methylphenyl sulfoxide 2e: m.p. 121-123 °C, m.p.[46] 122-124 °C. IR (KBr): 1024 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): 2.40 (s, 3 H), 4.0 (d, 1 H, J = 12.5 Hz), 4.10 (d, 1 H, J = 12.5 Hz), 7.01-7.05 (m, 2 H), 7.28-7.32 ppm (m, 7 H).

4-Bromobenzyl 4-methylphenyl sulfoxide 2f: m.p. 159-161 °C, m.p.[47] 161 °C. IR (KBr): 1030 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): 2.46 (s, 3 H), 3.99 (s, 2 H), 6.88 (d, 2 H, J = 8.2 Hz), 7.27-7.31 (m, 4 H), 7.42 ppm (d, 2 H, J = 8.2 Hz).

Benzyl 4-chlorophenyl sulfoxide 2g: m.p. 120-122 °C, m.p.[46] 120-122 °C). IR (KBr): 1036 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): 4.02 (d, 1 H, J = 12.5 Hz), 4.15 (d, 1 H, J = 12.5 Hz), 7.02 (d, 2 H, J = 6.8 Hz), 7.26-7.46 (m, 5 H), 7.36 ppm (d, 2 H, J = 6.8 Hz).

4-Bromobenzyl 4-chlorophenyl sulfoxide 2h: m.p. 134-136 °C, m.p.[45] 135-136 °C. IR (KBr): 1037 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): 3.98 (d, 1 H, J = 12.85 Hz), 4.05 (d, 1 H, J = 12.85 Hz), 6.87 (d, 2 H, J = 8.40 Hz), 7.30 (d, 2 H, J = 8.40 Hz), 7.45-7.51 ppm (m, 4 H).

4-Chlorophenyl 4-nitrobenzyl sulfoxide 2i: m.p. 154-155 °C, m.p.[47] 153.5-154.5 °C. IR (KBr): 1040, 1345, 1515 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 4.04 (d, 1 H, J = 12.83 Hz), 4.24 (d, 1 H, J = 12.83 Hz), 7.17 (d, 2 H, J = 8.53 Hz), 7.33 (d, 2 H, J = 8.53 Hz), 7.48 (d, 2 H, J = 8.53 Hz), 8.17 ppm (d, 2 H, J = 8.53 Hz).

Benzyl 4-bromobenzyl sulfoxide 2j: m.p. 139-140 °C. IR (KBr): 1028 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): 3.78 (d, 1 H, J = 13.09 Hz), 3.89 (d, 1 H, J = 13.09 Hz), 3.95 (s. 2 H), 7.2 (d, 2 H, J = 8.27 Hz), 7.32-7.33 (m, 2 H), 7.40-7.44 (m, 3 H), 7.54 ppm (d, 2 H, J = 8.27 Hz). Analysis Calcd. for C$_{14}$H$_{13}$SOBr C, 54.38; H, 4.24. Found: C, 54.0; H, 4.3.

Dibenzyl sulfoxide 2k: m.p. 131-133 °C, m.p.[48] 132-134 °C. IR (KBr): 1026 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): 3.91 (d, 2 H, J = 13.0 Hz), 3.98 (d, 2 H, J = 13.0 Hz), 7.31-7.41 ppm (m, 10 H).

Diphenyl sulfoxide 2l: m.p. 70-72 °C, m.p.[48] 69-72 °C. IR (KBr): 1038 cm^{-1}. ^{1}H NMR (CDCl$_3$, 200 MHz): 7.41-7.50 (m, 6 H), 7.61-7.66 ppm (m, 4 H).

Dibenzothiophene sulfoxide 5: m.p. 181-183 °C, m.p.[49] 181-183 °C. IR (KBr): 1038 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): 7.53-7.70 (m, 4 H), 7.83-8.04 ppm (m, 4 H).

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