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Halogenations of *S*-Benzyl-*S*-phenylsulfoximides and Base-induced Rearrangements of Their *N*- and α-Halo Derivatives to *N*-Sulfinylimines

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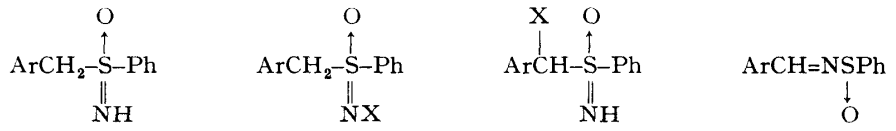
The reactions of *S*-benzyl- and *S*-(*p*-nitrobenzyl)sulfoximides **1a**, **b** with *N*-bromosuccinimide or *tert*-butyl hypochlorite gave the corresponding *N*-halosulfoximides **2a**, **b** or **3a**, **b**, respectively, in good yields. The *N*-bromo-*S*-(*p*-nitrobenzyl)sulfoximide **2b** decomposed in the presence of a light source to give the corresponding α-bromosulfoximide **4b**, whereas the other *N*-halosulfoximides **2a** and **3a**, **b** did not give the corresponding α-halosulfoximides **4a** and **5a**, **b**. On treatment with *N*-chlorosuccinimide, the *p*-nitrobenzylsulfoximide **1b** underwent both *N*- and α-chlorinations, while the benzylsulfoximide **1a** underwent only *N*-chlorination. The halosulfoximides **2**—**5** underwent base-induced rearrangements under various conditions to give the corresponding *N*-sulfinylimines **6** *via* the same three-membered cyclic sulfoximide intermediate, a thiazirine *S*-oxide **8**.

Keywords——halogenation; *N*-halosulfoximide; α-halosulfoximide; rearrangement; *N*-sulfinylimine (*N*-alkylidenesulfinamide); three-membered cyclic sulfoximide; thiazirine *S*-oxide

Because *N*-halosulfoximides have been used as halogenating agents in the halogenations of sulfoxides,[1] toluene,[2] and olefins,[3] it was expected that *N*-halosulfoximide containing an active methylene or a benzyl group would undergo rearrangement of the halogen atom to the active site.

In fact, we have recently reported the rearrangement of *N*-halosulfoximide derivatives having an α-methylene group activated with a 1,2-benzisoxazole ring to yield the corresponding α-halosulfoximides,[4] and we also found that these *N*- and α-halosulfoximides underwent novel base-induced rearrangement to give the same *N*-sulfinylimines.[5] In order to examine the generality of these interesting chemical properties of the *S*-[(1,2-benzisoxazol-3-yl)methyl]-sulfoximides, we examined the *S*-benzyl system and obtained similar results. Thus, this paper deals with the halogenations of *S*-benzyl-*S*-phenylsulfoximides **1** and the rearrangements of their *N*- and α-halo derivatives **2**—**5** into the corresponding *N*-sulfinylimines, *N*-benzylidenebenzenesulfinamides **6**.



1 **2**: X=Br; **3**: X=Cl **4**: X=Br; **5**: X=Cl **6**

a: Ar=Ph; **b**: Ar=*p*-NO_2Ph

Chart 1

Halogenations of the Free Sulfoximides 1a, b

The reactions of **1a**, **b** with *N*-bromosuccinimide (NBS) or *tert*-butyl hypochlorite (BHC) for 5—10 min at room temperature gave the corresponding *N*-halosulfoximides **2a**, **b** or **3a**, **b**, respectively, in isolated yields of 73—90%: all the reactions were quantitative. The reaction of the *p*-nitrobenzylsulfoximide **1b** with NBS, however, was allowed to continue for 7 h in the

presence of a light source (a room light), affording the α-bromosulfoximide **4a** in 30% yield instead of **2b**.

These findings suggest that the α-bromosulfoximide **4b** was produced *via* a facile *N*-bromination followed by bromine transfer reaction of the resulting *N*-bromosulfoximide **2b**. As shown in Table I, in fact, the *N*-bromosulfoximide **2b** decomposed at room temperature in the presence of a light source to give the α-bromosulfoximide **4b** in a yield (16—36%) that was dependent on the solvent used. In the early stages of the reactions examined, there was a clear indution period in which the liberation of bromine was observed. In the absence of a light source no decomposition occurred.

Table I. Decomposition of the *N*-Bromosulfoximide **2b**[a]

Reaction conditions	Products and yield (%)[b]	
	1b	**4b**
CH_2Cl_2, 24 h	27.8	36.9
1% EtOH–$CHCl_3$,[c] 10 h	57.5	24.0
5% EtOH–$CHCl_3$,[c] 5 h	72.9	16.0
1% EtOH–$CHCl_3$, dark, 1 week	No decomposition	

a) The reaction was carried out at room temperature in the presence of a room light unless otherwise noted.
b) Yields were determined by HPLC. *p*-Nitrobenzyl bromide was also obtained in 5—8% yield as another characterizable product.
c) Chloroform containing 1% or 5% ethanol.

The results described above suggest that the rearrangement of the *N*-bromosulfoximide **2b** was photochemically initiated and the molecular bromine formed during the induction period should act as the active brominating species.

On the other hand, the other *N*-halosulfoximides **2a** and **3a, b** decomposed in the presence of a light source, as with **2b**, to give **1a, b** in *ca.* 80% yields, but they did not give the corresponding α-halosulfoximides **4a** and **5a, b** as isolable, characterizable products (see "Experimental").

The *p*-nitrobenzylsulfoximide **1b** underwent both *N*- and α-chlorinations on treatment with *N*-chlorosuccinimide (NCS) as shown in Table II. This reaction proceeded either in the presence or in the absence of a light source, though the absence of a light source appears to retard the rate and to increase the yield of the α-chlorosulfoximide **5b**.

Table II. Reaction of the *p*-Nitrobenzylsulfoximide **1b** with NCS[a]

Reaction conditions	Products and yield (%)[b]		
	3b	**5b**	**1b** (recovered)
CH_2Cl_2, 24 h	—	45.9	47.2
1% EtOH–$CHCl_3$, 24 h	—	38.2	51.2
5% EtOH–$CHCl_3$, 24 h	—	48.4	44.2
CH_2Cl_2, dark, 48 h	—	60.2	34.9
1%EtOH–$CHCl_3$, dark, 48 h	—	52.9	40.1
5%EtOH–$CHCl_3$, dark, 48 h	—	55.7	40.4
$CDCl_3$, 15 h[c]	(33)	(35)	
$CDCl_3$, dark, 24 h[d]	(32)	(42)	

a) The reaction was carried out at room temperature in the presence of a room light unless otherwise noted.
b) Yields were determined by HPLC after the treatment described in "Experimental," during which **3b** was converted to **1b**, and those in parentheses were determined by NMR using the reaction mixture without any treatment.
c) The reaction was approximately 73% completed: prolonged reaction caused partial decomposition of **3b**.
d) The reaction was approximately 77% completed: prolonged reaction caused partial *N*-chlorination of **5b**.

On the basis of the results described above, the α-chlorination of **1b** with NCS seems to proceed through the direct α-attack of NCS.

On the other hand, the benzylsulfoximide **1a** underwent only *N*-chlorination on treatment with NCS, and the reaction required over a week for completion at room temperature.

In the α-halogenations of the sulfoximide derivatives examined in the previous[4] and present papers, the order of reactivity is *S*-(1,2-benzisoxazol-3-yl)methyl-> *S*-*p*-nitrobenzyl- (**1b**)> *S*-benzylsulfoximide (**1a**), suggesting that the reactivity is controlled by the degree of activation of the α-position, *i.e.*, α-CH acidity.

Alternative attempts to prepare the α-halosulfoximides **4a** and **5a** according to the method of Johnson and Corkins,[6] which involves amination of the corresponding α-halosulfoxides with *O*-mesitylenesulfonylhydroxylamine and α-chlorination of the corresponding *N*-halosulfoximides with BHC, were unsuccessful.

Base-induced Rearrangements of the Halosulfoximides 2—5

As with the halo derivatives of *S*-[(1,2-benzisoxazol-3-yl)methyl]sulfoximides,[5] the halosulfoximides **2**—**5** underwent base-induced rearrangements to give the corresponding *N*-sufinylimines **6**. The structure of **6** was confirmed by direct comparison with samples which were alternatively prepared according to the method of Davis *et al.*,[7] including oxidation of the corresponding *N*- sulfenylimines **7** with *m*-chloroperbenzoic acid in a two-phase system containing chloroform and water–sodium bicarbonate. The results of these rearrangements are summarized in Table III.

Table III. Rearrangements of the Halosulfoximides **2**—**5** with Base[a]

Compd.	Reaction conditions	Product (s) and yield (%)[b]			
2a	DBU (2 eq), 10 min	**6a**	54	**1a**	38
2a	K_2CO_3 (5 eq), 24 h	**6a**	81.5		
2b	DBU (1.2 eq), 10 min	**6b**	62	**1b**	26
2b	K_2CO_3 (3 eq), 10 h	**6b**	78		
3a	DBU (2 eq), 5 min	**6a**	93		
3a	K_2CO_3 (5 eq), 24 h	**6a**	55 (85)[c]		
3b	DBU (1.2 eq), 5 min	**6b**	94.5		
3b	K_2CO_3 (3 eq), 3 h	**6b**	96		
4b	DBU (3 eq), 4 h	**6b**	65 (76.5)[c]		
5b	DBU (3 eq), 5 h	**6b**	10[d]		

a) The reaction was carried out in dichloromethane at room temperature.
b) Isolated yields after column chromatography.
c) Based on the unrecovered halosulfoximide.
d) Under reflux in chloroform. The recovery of **5b** was 78%.

All the *N*-halosulfoximides **2a**, **b** and **3a**, **b** underwent rearrangement on treatment either with 1,5-diazabicyclo[5.4.0]-5-undecene (DBU) or with potassium carbonate at room temperature to give **6a**, **b** in good to excellent yields under various conditions. The α-bromosulfoximide **4b** was treated with 3 molar eq. of DBU at room temperature for 4 h to give **6b** in good yield. Under the same mild conditions, however, the α-chlorosulfoximide **5b** underwent no rearrangement, but under reflux in chloroform for 5 h, **5b** gave **6b** in 10% yield.

When the reactions of the *N*-chlorosulfoximides **3a**, **b** with DBU were carried out in chloroform-d_1 ($CDCl_3$), **3a**, **b** underwent partial hydrogen-deuterium exchange of the methylene protons with the deuterium of $CDCl_3$ together with the rearrangement: in the nuclear magnetic resonance (NMR) spectra of the reaction mixtures the peak height of non-deuterated chloroform increased 2—4 times as compared with the original peak height. Similarly, under the same conditions the α-bromosulfoximide **4b** underwent patrial H-D exchange together with

the rearrangement, whereas the α-chlorosulfoximide **5b** underwent only H-D exchange. These findings suggest the formation of the α-carbanion under the rearrangement conditions.

On the basis of the results described above, these rearrangements may proceed in a manner similer to that of the Never[8] or Ramberg–Backlund[9] reaction to afford as an intermediate a three-membered cyclic sulfoximide, *i.e.*, a thiazirine *S*-oxide **8**,[5] followed by spontaneous ring opening without loss of the sulfur component to give **6** (Chart 2).

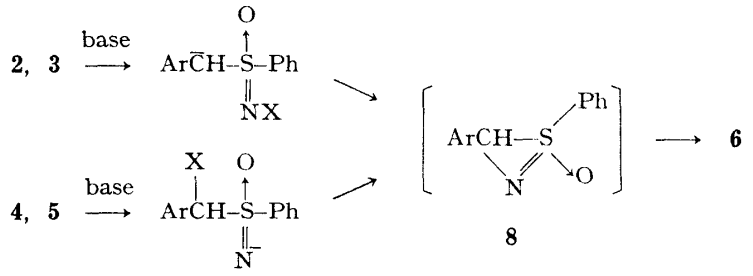


Chart 2

Thus, it has become apparent in the previous[5] and present papers that halosulfoximides having an α-active methylene or a benzyl group readily undergo rearrangements under mild conditions to give the corresponding *N*-sulfinylimines. Although *N*-sulfinylimines (*N*-alkylidenesulfinamides) are a relatively new family of reactive sulfur compounds, they have been synthesized by several procedures[7b,10] and demonstrated to be useful intermediates for organic syntheses,[5,7b,11] including a mild, high-yield route to unstable sulfenic acids.[7b,12]

Experimental

All melting points were measured on an Ishii micro melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian EM-360 spectrometer with tetramethylsilane as an internal standard in $CDCl_3$. The following abbreviations are used: s, singlet; d, doublet; m, multiplet. Infrared (IR) spectra were taken in KBr disks with a Hitachi EPI-G3 spectrophotometer. High performance liquid chromatography (HPLC) was carried out on a Waters 204 machine using a Nucleosil $_{10}C_{18}$ column with 3% aq. AcOH–EtOH (55: 45) as an eluent.

***S*-Benzyl- and *S*-(*p*-Nitrobenzyl)-*S*-phenylsulfoximides (1a, b)**——The free sulfoximides **1a**, **b** were prepared from the corresponding sulfoxides[13] and *O*-mesitylenesulfonylhydroxylamine.[14] **1a**: mp 109—112°C (CH_2Cl_2–isopropyl ether). *Anal.* Calcd for $C_{13}H_{13}NOS$: C, 67.50; H, 5.66; N, 6.06; S, 13.86. Found: C, 67.41; H, 5.55; N, 5.95; S, 13.84. NMR δ: 2.80 (1H, s, NH), 4.34 (2H, s, CH_2), 6.9—8.0 (10H, m, arom.). IR ν cm^{-1}: 3320 (NH), 1216, 1109, 972 (NSO). **1b**: mp 163—165°C (CH_2Cl_2–isopropyl ether). *Anal.* Calcd for $C_{13}H_{12}N_2O_3S$: C, 56.51; H, 4.38; N, 10.14; S, 11.60. Found: C, 56.32; H, 4.31; N, 10.22; S, 11.60. NMR δ: 2.92 (1H, s, NH), 4.44 (2H, s, CH_2), 7.1—8.0 m, 7.30 (7H, d, J=9.0 Hz, arom.), 8.15 (2H, d, J=9.0 Hz, arom.). IR ν cm^{-1}: 3325 (NH), 1513, 1345 (NO_2), 1224, 1109, 940 (NSO).

***N*-Halo-*S*-benzyl-*S*-phenylsulfoximides 2a, b and 3a, b. Reactions of 1a, b with NBS or BHC**——**2a** and **3a**: An equimolar amount of NBS or BHC was added to a solution of **1a** (1.0 g) in CH_2Cl_2 (10 ml) at room temperature and the mixture was stirred for 5 min in the dark. The reaction mixture was directly subjected to silica gel column chromatography using $CHCl_3$ as an eluent to give **2a** or **3a** in 90% or 88% yield, respectively. Recrystallization from CH_2Cl_2–hexane gave pure products. **2a**: mp 97—105°C. *Anal.* Calcd for $C_{13}H_{12}BrNOS$: C, 50.33; H, 3.90; Br, 25.76; N, 4.52; S, 10.33. Found: C, 50.24; H, 3.84; Br, 25.54; N, 4.24; S, 10.18. NMR δ: 4.68, (2H, s, CH_2), 6.9—7.9 (10H, m, arom.). IR ν cm^{-1}: 1212, 1089, 971 (NSO). **3a**: mp 86—89°C. *Anal.* Calcd for $C_{13}H_{12}ClNOS$: C, 58.75; H, 4.55; Cl, 13.34; N, 5.27; S, 12.06. Found: C, 58.63; H, 4.56; Cl, 13.56; N, 5.24; S, 12.09. NMR δ: 4.61 (2H, s, CH_2), 6.9—7.9 (10H, m, arom.). IR ν cm^{-1}: 1212, 1089, 973 (NSO).

2b and **3b**: After a mixture of equimolar amounts of **1b** (1.0 g) and NBS or BHC in $CHCl_3$ (10 ml) had been stirred for 10 min at room temperature in the dark, the precipitates were collected by filtration and washed with cold $CHCl_3$ to give **2b** or **3b** in 86% or 73% yield, respectively. Recrystallization from CH_2Cl_2–isopropyl ether gave pure products. **2b**: mp 131—133°C. *Anal.* Calcd for $C_{13}H_{11}BrN_2O_3S$: C, 43.96; H, 3.12; Br, 22.50; N, 7.89; S, 9.03. Found: C, 44.13; H, 2.93; Br, 22.71; N, 7.89; S, 8.78. NMR δ: 4.70 (2H, s, CH_2), 7.24 d, 8.09 (each 2H, d, J=8.6 Hz, NO_2Ph), 7.4—7.9 (5H, m, Ph). IR ν cm^{-1}: 1512, 1344 (NO_2),

1212, 1089, 973 (NSO). **3b**: mp 128—130°C. *Anal.* Calcd for $C_{13}H_{11}ClN_2O_3S$: C, 50.25; H, 3.57; Cl, 11.41; N, 9.01; S, 10.32. Found: C, 50.18; H, 3.63; Cl, 11.21; N, 8.92; S, 10.24. NMR δ: 4.71 (2H, s, CH_2), 7.25, d, 8.09 (each 2H, d, J=9.0 Hz, NO_2Ph), 7.4—7.9 (5H, m, Ph). IR ν cm^{-1}: 1512, 1342 (NO_2), 1216, 1088, 972 (NSO).

When the above reactions were carried out in $CDCl_3$ at room temperature, NMR analyses of the reaction mixtures showed that the yields of the *N*-halosulfoximides **2** and **3** were quantitative.

***S*-(α-Bromo-*p*-nitrobenzyl)-*S*-phenylsulfoximide 4b. Prolonged Reaction of 1b with NBS**——A slight excess of NBS was added to a stirred solution of **1b** (2.0 g) in $CHCl_3$ (50 ml) and the resulting mixture was stirred for 7 h at room temperature under a room light. The reaction mixture was washed with dilute aq. K_2CO_3, then the organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was chromatographed on a silica gel column using $CHCl_3$ as an eluent to afford 0.8 g (30% yield) of **4b** together with 0.9 g of recovered **1b**. The NMR spectrum of **4b** showed it to be a mixture of diastereomers: two distinct methine singlets were observed. **4b**: mp 116—124°C (CH_2Cl_2–isopropyl ether). *Anal.* Calcd for $C_{13}H_{11}BrN_2O_3S$: C, 43.96; H, 3.12; Br, 22.50; N, 7.89; S, 9.03. Found: C, 44.06; H, 3.13; Br, 22.23; N, 7.86; S, 9.16. NMR δ: 3.3 s, 3.6 (1H, s, NH), 5.77 s, 5.81 (1H, s, CH), 7.25—8.3 (9H, m, arom.). IR ν cm^{-1}: 3275 (NH), 1513, 1346 (NO_2), 1242, 1135, 950 (NSO).

Decomposition Reactions of the *N*-Halosulfoximides 2 and 3——The reaction was carried out with a 0.05 M solution of the *N*-halosulfoximide. After an appropriate reaction time, an aliquot (1—2 ml) of the reaction mixture was taken up, washed with 5% aq. K_2CO_3 (5 ml), and extracted with $CHCl_3$ (5 ml). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in 1 ml of $CHCl_3$ and 19 ml of EtOH, and then subjected to HPLC analysis.

The results for the decomposition of *N*-bromo-*S*-(*p*-nitrobenzyl)-*S*-phenylsulfoximide **2b** are summarized in Table I. The other *N*-halosulfoximides **2a** and **3a, b** decomposed in 7 h, 55 h, and 24 h, respectively, in 5% EtOH–$CHCl_3$ to give **1a, b** in *ca.* 80% yields together with a small amount of the corresponding benzyl halide, but no other characterizable products were obtained.

Reactions of 1a, b with NCS——**1a**: The reaction of **1a** (60 mg) with an equimolar amount of NCS was carried out in $CDCl_3$ (1 ml) at room temperature in a sealed tube in the dark. After a week, NMR analysis of the reaction mixture indicated that the reaction was approximately 88% completed, and the yield of the *N*-chlorosulfoximide **3a** was *ca.* 84%.

1b: The results for the reaction of **1b** with NCS are summarized in Table II. The reaction was carried out using a 0.1—0.3 M solution of **1b** with an equimolar amount of NCS. HPLC analysis was run after the reaction mixture had been worked up as described above. NMR analysis was carried out directly on the reaction mixture without any treatment. *S*-(α-Chloro-*p*-nitrobenzyl)-*S*-phenylsulfoximide **5b** was isolated as a mixture of diastereomers by silica gel column chromatography and recrystallized from CH_2Cl_2-isopropyl ether: mp 125—131°C. *Anal.* Calcd for $C_{13}H_{11}ClN_2O_3S$: C, 50.25; H, 3.57; Cl, 11.41; N, 9.01; S, 10.32. Found: C, 49.99; H, 3.46; Cl, 11.57; N, 8.93; S, 10.36. NMR δ: 3.3 (1H, s, NH), 5.74 s, 5.77 (1H, s, CH), 7.3—8.1 (7H, m, arom.), 8.18 (2H, d, J=9.0 Hz, arom.). IR ν cm^{-1}: 3275 (NH), 1515, 1347 (NO_2), 1242, 1137, 952 (NSO).

***N*-Benzylidene- and *N*-(*p*-Nitrobenzylidene)benzenesulfinamides (6a, b). Rearrangement Reactions of the Halosulfoximides 2—5 with Base**——The reaction was carried out with a 0.1—0.2 M solution of the halosulfoximide under the conditions stated in Table III: the reaction of the *N*-halosulfoximide with K_2CO_3 was carried out in the dark in order to avoid partial decomposition of the *N*-halosulfoximide as described above. After an appropriate reaction time, the reaction mixture was directly subjected to silica gel column chromatography and eluted with $CHCl_3$ to give **6**. **6a**: mp 80—83°C (hexane) (lit.[7b] mp 78—79 °C). *Anal.* Calcd for $C_{13}H_{11}NOS$: C, 68.10; H, 4.84; N, 6.11; S, 13.98. Found: C, 68.35; H, 4.75; N, 6.11; S, 14.05. NMR δ: 7.2—8.1 (10H, m, arom.), 8.79 (1H, s, CH=N). IR ν cm^{-1}: 1604 (C=N), 1099 (SO). **6b**: mp 154—157°C (CH_3CN). *Anal.* Calcd for $C_{13}H_{10}N_2O_3S$: C, 56.92; H, 3.67; N, 10.21; S, 11.69. Found: C, 57.30; H, 3.72; N, 10.45; S, 11.70. NMR δ: 7.3—7.9 (5H, m, Ph), 8.02 d, 8.30 (each 2H, d, J=9.0 Hz, NO_2Ph), 8.85 (1H, s, CH=N). IR ν cm^{-1}: 1590 (C=N), 1519, 1341 (NO_2), 1101 (SO).

Alternative Preparation of the *N*-Sulfinylimines 6a, b——*N*-Benzylidene- and *N*-(*p*-nitrobenzylidene)-benzenesulfenamides (**7a, b**) were prepared in 72% and 5% yields, respectively, according to the procedure of Davis *et al.*[7a] **7a**: mp 45—47°C (hexane) (lit.[10a] mp 44°C). *Anal.* Calcd for $C_{13}H_{11}NS$: C, 73.20; H, 5.20; N, 6.57; S, 15.03. Found: C, 72.93; H, 5.24; N, 6.50; S, 14.74. NMR δ: 7.1—8.1 (10H, m, arom.), 8.49 (1H, s, CH=N). **7b**: mp 80—81°C (EtOH) (lit.[10a] mp 83—84°C). *Anal.* Calcd for $C_{13}H_{10}N_2O_2S$: C, 60.45; H, 3.90; N, 10.85; S, 12.41. Found: C, 60.71; H, 4.11; N, 10.85; S, 12.44. NMR δ: 7.1—8.1 m, 7.74 (7H, d, J=9.0 Hz, arom.), 8.27 (2H, d, J=9.0 Hz, arom.), 8.48 (1H, s, CH=N).

The above *N*-sulfenylimines **7a, b** were oxidized in a two-phase system containing chloroform and water-sodium bicarbonate with *m*-chloroperbenzoic acid to give **6a, b** in 93% and 77% yields, respectively, according to the method of Davis *et al.*[7b,c] The IR and NMR spectra of these samples were in agreement with those of the products of the rearrangements of the halosulfoximides **2**—**5** described above.

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