Syntheses and Reactions of Optically Active Alkyltoluene-*p*-sulphinamides. Part 2.[1] Substitution at Sulphur with Retention of Configuration

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The stereochemistry of the reaction of optically active sulphinamides (**1a**—**c**) with different alkylating agents has been examined. The electrophilic attack on sulphoximidate anions occurs only at nitrogen. Prevailing retention of configuration at sulphur (e.g. up to 48%) is observed in the formation of *p*-tolylsulphinyl acetates from sulphinamides (**1b**—**c**) with α-bromo esters.

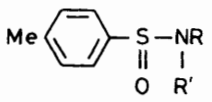
In recent years much attention has been given to the mechanistic aspects of nucleophilic substitutions at di-, tri-, and tetra-co-ordinate sulphur.[2] In particular, the study has been extended to sulphinamides, which constitute a suitable trico-ordinated substrate, in view of their synthetic importance. They have been used *inter alia* for preparing optically active sulphoxides,[2] sulphinates,[2] and, very recently, thiosulphinates.[3] Most of the nucleophilic substitutions at the sulphinyl group of sulphinamides take place with full or predominant inversion of configuration, but there are also a few examples of reactions that occur with retention of configuration.[1,2]

In this paper we report the results of our investigation of the stereochemistry of alkylation of *N*-alkyltoluene-*p*-sulphinamides and the configurational stability of the anions produced by their deprotonation or that of their reaction products. *N*-Deprotonated sulphinamides are formally tridentate anions since electrophilic attack may involve reaction at nitrogen, sulphur, or oxygen. For this reason we have also examined the behaviour of sulphoximidate anions with electrophilic agents in order to discover whether they are O, N, or S nucleophiles.

The structure of the reaction products has been confirmed by independent syntheses and/or by their mass spectra [fast atomic bombardment (f.a.b.) spectra] for labile compounds. Enantiomeric excesses (e.e.) have been determined by ^{1}H n.m.r. spectroscopy in the presence of Eu(hfc)$_3$ as chiral shift reagent, or by comparison of their optical rotations with those reported in the literature.

The starting sulphinamides (**1a**—**c**) were prepared by the classical procedure[4] from (−)-(*S*)-methyl toluene-*p*-sulphinate and amide ions obtained from the amines and Grignard reagents or alkyl-lithiums. They have the (+)-(*S*) configuration, since the reaction occurs with inversion of configuration at sulphur.[4a] Conditions, yields, and e.e. values are given in Table 1.

The first reaction examined was the alkylation of substrates (**1a**—**c**) with methyl iodide and allyl bromide. Use of benzyl



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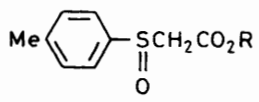

(8) R = Bu^t
(9) R = Et

	R	R′
(1a)	Ph	H
(1b)	$CH(Me)_2$	H
(1c)	$CH_2CH{=}CH_2$	H
(2a)	Ph	Me
(2b)	$CH(Me)_2$	Me
(2c)	$CH_2CH{=}CH_2$	Me
(3a)	Ph	$CH_2CH{=}CH_2$
(3b)	$CH(Me)_2$	$CH_2CH{=}CH_2$
(3c)	$CH_2CH{=}CH_2$	$CH_2CH{=}CH_2$
(4a)	Ph	$CH_2CO_2Bu^t$
(4b)	$CH(Me)_2$	$CH_2CO_2Bu^t$
(4c)	$CH_2CH{=}CH_2$	$CH_2CO_2Bu^t$
(5b)	$CH(CH_3)_2$	CH_2CO_2Et
(5c)	$CH_2CH{=}CH_2$	CH_2CO_2Et
(6b)	$CH(Me)_2$	COMe
(6c)	$CH_2CH{=}CH_2$	COMe
(7b)	$CH(Me)_2$	COPh

Table 1. Optically active sulphinamides (**1a**—**c**)

Substrate	Reaction time	Yield (%)	$[\alpha]_D^{25}$ [a]	E.e. (%)
(1a)	30 min	60	+199.9°	89
(1b)	4 h	66	+167.4°	100
(1c)	4 h	55	+145.5°	100

[a] *c* = 1.0 In chloroform.

Table 2. Alkylation of optically active *N*-substituted sulphinamides

Substrate	Alkylating agent	Reaction time	Temp. (°C)	Product	Yield (%)	$[\alpha]_D^{25}$ [a]	E.e. (%)
(1a)	MeI	30 min	−70	**(2a)**	100	−48.3°	47
(1a)[b]	$CH_2{=}CHCH_2Br$	24 h	−70	**(3a)**	96	−19.1°	*c*
(1b)	MeI	2.5 h	0	**(2b)**	100	+92.1°	33
(1b)	$CH_2{=}CHCH_2Br$	78 h	0	**(3b)**	9	+21.4°	*c*
(1c)	MeI	24 h	0	**(2c)**	82	+108.3°	84
(1c)	$CH_2{=}CHCH_2Br$	5 h	0	**(3c)**	71	+53.0°	100

[a] *c* = 1.0 In chloroform. [b] The starting sulphinamide had e.e. 44%. [c] E.e. unknown, because of instability of the product.

Table 3. Optically active *N,N*-disubstituted sulphinamides

Reaction time (h)	Products	Yield (%)	$[\alpha]_D^{25}$ [a]	E.e. (%)
20	(**2a**)	27	−5.64°	5
22	(**2b**)	26	+85.9°	31
18	(**2c**)	62	+57.3°	45
2	(**3a**)	91	−16.4°	*b*
2	(**3c**)	89	+49.2°	93

[a] *c* = 1.0 In chloroform. [b] The e.e. is unknown, because of the instability of the product.

Table 4. Sulphinamides

Compound (Formula)	M.p. (°C)	Mass	Found (%) (required) C	H	N
(**1b**)	73—75		60.85	7.6	7.05
($C_{10}H_{15}NOS$)			(60.91)	(7.61)	(7.11)
(**1c**)	38—40		61.5	6.6	7.25
($C_{10}H_{13}NOS$)			(61.54)	(6.67)	(7.18)
(**3a**)	59—63	271	70.7	6.35	5.05
($C_{16}H_{17}NOS$)			(70.85)	(6.27)	(5.17)
(**2b**)		211	62.5	8.0	6.7
($C_{11}H_{17}NOS$)			(62.56)	(8.06)	(6.64)
(**3b**)		237	65.3	8.0	5.85
($C_{13}H_{19}NOS$)			(65.81)	(8.02)	(5.91)
(**2c**)		209	63.3	7.25	6.75
($C_{11}H_{15}NOS$)			(63.16)	(7.18)	(6.70)
(**3c**)		235	66.4	7.15	5.9
($C_{13}H_{17}NOS$)			(66.38)	(7.23)	(5.96)
(**4a**)			66.5	6.6	4.1
($C_{19}H_{23}NOS$)			(66.09)	(6.67)	(4.06)
(**4b**)			61.7	8.0	4.3
($C_{16}H_{25}NOS$)			(61.74)	(8.04)	(4.50)
(**4c**)		309	62.1	7.45	4.5
($C_{16}H_{23}NOS$)			(62.14)	(7.44)	(4.53)
(**5b**)		251	66.9	8.4	5.6
($C_{14}H_{21}NOS$)			(66.93)	(8.37)	(5.58)
(**5c**)			67.5	7.6	5.65
($C_{14}H_{19}NOS$)			(67.47)	(7.63)	(5.62)
(**6b**)	38—40		60.3	7.0	5.8
($C_{12}H_{17}NO_2S$)			(60.25)	(7.11)	(5.86)
(**7b**)	66—69		67.7	6.35	4.55
($C_{17}H_{19}NO_2S$)			(67.77)	(6.31)	(4.65)
(**6c**)			60.7	6.3	5.85
($C_{12}H_{15}NO_2S$)			(60.76)	(6.33)	(5.91)

bromide and α-methylbenzyl bromide was abandoned after a few preliminary experiments since the first led to a complex reaction mixture and the second was too unreactive. Reactions were performed by adding at −70 °C or at 0 °C the alkylating agent to the solution of the lithium salt of the sulphinamide, generated *in situ* with BuLi at −70 °C—0 °C. Reaction conditions, chemical and optical yields, and optical rotations are in Table 2.

The highest enantioselectivities have been obtained starting from *N*-allyltoluene-*p*-sulphinamide (**1c**): alkylated sulphinamides (**3c**) and (**2c**) are 100% and 68% optically pure, respectively. In the case of *N*-isopropyltoluene-*p*-sulphinamide (**1b**), the reaction with methyl iodide has a lower stereoselectivity (33% e.e.) in forming compound (**2b**); with allyl bromide the product (**3b**) is of unknown optical purity because of its instability. All reactions are totally regioselective since only *N*-alkylation products were obtained in high chemical yield.

Optically active *N,N*-disubstituted sulphinamides have also been prepared from (−)-(*S*)-methyl toluene-*p*-sulphinate with the lithium salt of a suitable amine. When we applied this procedure to the synthesis of the sulphinamides (**2a**) and (**2c**), both chemical and optical yields were lower than those obtained in the alkylation reaction (Table 3). On the contrary, for compounds (**2b**) and (**3c**) both methods gave similar results. The *N,N*-dialkyl sulphinamides gave stable molecular ions in mass spectrometry, in contrast to *N,N*-diaryl sulphinamides which could be characterized only by the f.a.b. technique (Table 4). We have also examined the reactivity of sulphoximidate anions towards acyl halides such as benzoyl chloride and acetyl chloride. Similar reactions with the lithium salts of racemic sulphinamides have already been reported in the literature.[5] Isopropyltoluene-*p*-sulphinamide anion generated from (**1b**) with BuLi in THF afforded the optically active derivatives (**6b**) and (**7b**). Reaction conditions, yields, and optical rotations are in Table 5. Sulphinamide (**1c**) gave only the acetyl derivative (**6c**) whereas the analogous reaction with benzoyl chloride gave a complex mixture of products. Acyl sulphinamides (**6b**), (**6c**), and (**7c**), have been characterized by ^1H n.m.r. and i.r. spectroscopy. In this case also, only *N*-alkylation is occurring.

Acyl sulphinamides are chemically unstable and decompose on standing even at −20 °C; this prevented the determination of e.e. values with $Eu(hfc)_3$ as chiral shift reagent and their identification by mass spectroscopy. It is likely that the presence of two electron-withdrawing groups on the nitrogen makes easier the breaking of S–N bond. The absence of substantial racemization of the starting sulphinamides during the acylation reaction is notable; recovered isopropyltoluene-*p*-sulphinamide (**1b**) had 91% e.e.

The anions of optically active sulphinamides (**1a—c**) have also been treated with α-bromo esters, in particular with t-butyl and ethyl α-bromoacetates. To our surprise, as well as the *N*-alkylated products (**4a—c**), optically active sulphinyl acetates (**8**) and (**9**) were obtained from sulphinamides (**1b**) and (**1c**). Phenyl- (**1a**), isopropyl- (**1b**), and allyl-toluene-*p*-sulphinamides (**1c**) were recovered, with 29%, 83%, and 91% e.e., respectively. The structures of compounds (**4a—c**) were confirmed by f.a.b. mass spectrometery and that of (**8**) and (**9**) by mass spectrometery. Reaction conditions, yields, optical rotations, and e.e. are in Tables 6 and 7.

Table 5. Acylation of optically active sulphinamides

Substrate	Reaction time	Temp. (°C)	Product	Yield (%)	$[\alpha]_D^{25}$ [a]	E.e (%)
(**1b**)	1 h	0	(**7b**)	61	−154.1°	*b*
(**1b**)	*c*	*c*	(**6b**)	41	+21.1°	*b*
(**1c**)	15 min	−70	(**6c**)	98	−9.7°	*b*

[a] *c* = 1.0 In chloroform. [b] The e.e. are unknown, because of the instability of the products. [c] For 24 h at −70 °C, then for 6 h at 0 °C.

Table 6. Alkylation of optically active sulphinamides (**1**) with α-bromo esters

Substrate	R	Reaction time	Temp. (°C)	Product	Yield (%)	$[\alpha]_D^{25}$ [a]	E.e. (%)
(**1a**)	Bu^t	15 min	−70	(**4a**)	16	−6.9°	*b*
(**1b**)	Bu^t	1.5 h	−70	(**4b**)	13	−1.1°	100
(**1b**)	Bu^t	40 h	−70	(**4b**)	16	−11°	100
(**1b**)	Bu^t	5 h	0	(**4b**)	13	−11°	100
(**1b**)	Et	3 h	−70	(**5b**)	5	−3.1°	*b*
(**1b**)	Et	5 h	0	(**5b**)	3	−3.6°	*b*
(**1c**)	Bu^t	1.5 h	−70	(**4c**)	22	−0.3°	*b*
(**1c**)	Et	5 h	0	(**5c**)	7	+2.7°	*b*

[a] *c* = 1.0 in chloroform. [b] The e.e. is unknown, because of the instability of the product.

Table 7. Optically active sulphinyl acetates

Substrate	R	Reaction time (h)	Temp. (°C)	Product	Yield (%)	$[\alpha]_D^{25}$ [a]	E.e. (%)
(**1b**)	Bu^t	1.5	−70	(**8**)	10	+23.7°[a]	16[b]
(**1b**)	Bu^t	40	−70	(**8**)	22	+7.1°[a]	5[b]
(**1b**)	Bu^t	5	0	(**8**)	6	+8.6°[a]	6[b]
(**1c**)	Bu^t	1.5	−70	(**8**)	9	+16.4°[a]	11[b]
(**1b**)	Et	3	−70	(**9**)	5	+55.2°[c]	29[d]
(**1b**)	Et	5	0	(**9**)	8	+91.7°[c]	48[d]
(**1c**)	Et	5	0	(**9**)	27	+24.4°[c]	13[d]

[a] Determined in ethanol. [b] Based on the highest literature[6] rotation. [c] Determined in acetone. [d] Based on the highest literature[7] rotation.

It is notable that, in spite of the low chemical yield, the alkylation of isopropyltoluene-*p*-sulphinamide (**1b**) with t-butyl α-bromoacetate to give (**4b**) is completely stereoselective both at −70 °C and at 0 °C.

Sulphinyl acetates (**8**) and (**9**) are formed with predominant retention of configuration. Their optical purity and absolute configurations have been determined by comparison with the data reported in the literature for the corresponding optically pure samples.[6,7] Their formation can be rationalized on the basis of nucleophilic substitution on sulphinamides (**1b**) and (**1c**) by the lithium acetates formed *in situ* by reaction of the α-bromo esters with butyl-lithium. The data of Table 7 show that retention of configuration at sulphur reaches its maximum in the reaction of isopropyltoluene-*p*-sulphinamide (**1b**) with ethyl α-bromoacetate at −70 °C (48% e.e.). The stereochemical path of this process is independent of the steric demand of the alkyl group of the α-bromo ester. As expected, when the reaction is carried out at a higher temperature, racemization in the formation of (+)-(**8**) and (+)-(**9**) is greater.

Retention of configuration at sulphur in such processes has been explained by Mikolajczyk[2] by an addition–elimination mechanism *via* a sulphurane intermediate, in which the entering and the leaving groups occupy axial and equatorial positions, respectively. By analogy with the acid-catalysed alcoholysis of (+)-*N*,*N*-di-isopropyltoluene-*p*-sulphinamide,[3] we think that in our case also the steric factors in the attacking and in the departing group in the sulphurane intermediate can be responsible for the observed retention of configuration in the formation of sulphinyl acetates (**8**) and (**9**).

Experimental

^{1}H N.m.r. spectra were recorded in $CDCl_3$ on a Varian 390 instrument, using TMS as internal standard. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. Enantiomeric excesses were determined by ^{1}H n.m.r. with the aid of $Eu(hfc)_3$ as shift reagent on a Varian XL 200 instrument preoptimised with the racemic compounds. A 5% molar equivalent of shift reagent generally gave satisfactory peak separation. Mass spectra were recorded on a 7070 EQ spectrometer equipped with an HF magnet and standard f.a.b. source, operating at 8 keV with xenon. (−)-(*S*)-Methyl toluene-*p*-sulphinate (Aldrich) had $[\alpha]_D^{20} = -202—2°$ (*c* 2 in acetone), m.p. 99—101 °C.

Synthesis of Optically Active N-*Alkyl- and* N-*Phenyl-sulphinamides* (**1a—c**). *General Procedure.*—Lithium di-isopropylamide (LDA) (1 mmol) in tetrahydrofuran (THF) was added to a stirred solution of amine (1 mmol) in THF at −30 °C, under nitrogen. The mixture was kept at −30 °C for 15 min and then added dropwise to a stirred solution of (−)-(*S*)-methyl toluene-*p*-sulphinate (1 mmol) in THF at −70 °C, under nitrogen. In the case of *N*-isopropyltoluene-*p*-sulphinamide, butyl-lithium was added instead of LDA. After an appropriate time (see Table 1) the mixture was quenched with saturated aqueous ammonium chloride, the aqueous phase was extracted with dichloromethane, and the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure. The crude product was purified by flash chromatography (in diethyl ether–light petroleum, 8:2 v/v). In the case of *N*-phenyltoluene-*p*-sulphinamide the crude product was purified by column chromatography (in diethyl ether–light petroleum 4:6 v/v). Details are in Table 1. *N*-Phenyltoluene-*p*-sulphinamide (**1a**) had m.p. 129.5—131.5 °C (lit.,[8] m.p. 129—130 °C). Data for *N*-isopropyltoluene-*p*-sulphinamide (**1b**) and *N*-allyltoluene-*p*-sulphinamide (**1c**) are in Table 4.

Alkylation of N-*Substituted Sulphinamides* (**1a—c**) *with Methyl Iodide and Allyl Bromide.*—Butyl-lithium (1.5 mmol) in hexane was added to a stirred solution of the sulphinamide (1 mmol) in THF at −30 °C, under nitrogen. The mixture was kept at −30 °C for 15 min, then methyl iodide or allyl bromide (1.5 mmol) was added at −70 °C, under nitrogen. After an appropriate time at −70 °C or 0 °C (see Table 2), the mixture was quenched with saturated aqueous ammonium chloride. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. This was purified by flash chromatography [in diethyl ether–light petroleum, 8:2 v/v, as eluant in the case of the allylation of (**1b**) and methylation of (**1c**), and in diethyl ether–light petroleum, 4:6 v/v, in the case of allylation of (**1c**)]. Compounds (**2a**), (**2b**), and (**3a**) were pure by thin layer chromatography. Details are in Table 2. *N*-Methyl-*N*-phenyltoluene-*p*-sulphinamide (**2a**) had m.p. 77—78 °C (lit.,[8] m.p. 79—80 °C). Data for N-*allyl*-N-*phenyltoluene*-p-*sulphinamide* (**3a**), N-*isopropyl*-N-*methyltoluene*-p-*sulphinamide* (**2b**), N-*allyl*-N-*isopropyltoluene*-p-*sulphinamide* (**3b**), and N,N-*diallyltoluene*-p-*sulphinamide* (**3c**) are reported in Table 4. Flash chromatography of compounds (**3c**) and (**3b**) also afforded the starting sulphinamides (**1c**) and (**1b**) in 20% and 60% chemical yields respectively, the e.e. values being 30% and 77%.

Alkylation of N-*Substituted Sulphinamides* (**1a—c**) *with α-Bromo Esters.*—Butyl-lithium (1.2 mmol) in hexane was added to a stirred solution of sulphinamide (1 mmol) in THF at −30 °C, under nitrogen. After 15 min the mixture was cooled to −70 °C, then the appropriate α-bromo ester (1 mmol) was added, and the reaction mixture was maintained at −70 °C or 0 °C (Table 6). The mixture was quenched with saturated aqueous ammonium chloride and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product, which was purified by flash chromatography (diethyl ether–light petroleum, 8:2 v/v, as eluant; in the case of product (**4a**) the eluant was diethyl ether–light petroleum, 1:1 v/v). Details are in Tables 4 and 6. In these reactions the recovered *N*-phenyl-, *N*-isopropyl-, and *N*-allyl-toluene-*p*-sulphinamides had 29%, 83%, and 91% e.e., respectively. In alkylations of (**1b**) and (**1c**) the (+)-alkyl tolylsulphinylacetates (**8**) and (**9**) were also recovered; chemical and optical yields are in Table 7.

Acylation of N-*Substituted Sulphinamides* (**1b**) *and* (**1c**).—Butyl-lithium (1.2 mmol) in hexane was added to a stirred solution of the sulphinamide (1 mmol) in THF at −30 °C, under nitrogen. After 15 min the mixture was kept at −70 °C, and the acylating agent (1 mmol) was added. After an appropriate time at −70 °C or 0 °C (Table 5), the mixture was quenched with saturated aqueous ammonium chloride. The

aqueous phase was extracted with CH_2Cl_2 and the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. Flash chromatography [in diethyl ether–light petroleum, 4:6 v/v, in the case of benzoylation of (**1b**), and in diethyl ether–light petroleum, 7:3 v/v, in the case of acetylation of (**1b**)] gave the products (Table 5). The crude product of acetylation of (**1c**) was pure by t.l.c. while benzoylation of sulphinamide (**1c**) afforded a complex mixture of products that were not identified. Reaction time, reaction temperature, chemical and optical yields are reported in Table 5. Data for N-*acylsulphinamides* (**6b**) and (**7b**) are in Table 4.

Synthesis of Optically Active N,N-*Disubstituted Sulphinamides. General Procedure.*—Lithium di-isopropylamide (1 mmol) in THF was added to a stirred solution of amine (1 mmol) at −30 °C, under nitrogen. The mixture was kept at this temperature for 15 min and then added dropwise to a stirred solution of (−)-(*S*)-methyl toluene-*p*-sulphinate (1 mmol) in THF at −70 °C, under nitrogen. After an appropriate time at this temperature (Table 3) the mixture was quenched with saturated aqueous ammonium chloride. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product, purified by flash chromatography [in diethyl ether–light petroleum, 6:4 v/v, in the case of compounds (**2c**) and (**3c**)]. The crude products (**2a**) and (**3a**) were purified using diethyl ether–light petroleum, 1:1 v/v, as eluant, and diethyl ether–light petroleum, 8:2 v/v, in the case of (**2b**). Details are in Table 3. Compounds (**2b**), (**2c**), and (**3c**) were characterized by comparison with authentic samples.

Synthesis of Racemic Sulphinamides (**1a**) *and* (**3a**).—Racemic sulphinamide (**1a**) was prepared by reaction of toluene-*p*-sulphinyl chloride (1 mmol) with aniline (2 mmol) in anhydrous diethyl ether at 20 °C for 30 min. The usual work-up gave the crude product which was purified by column chromatography (in diethyl ether–light petroleum, 4:6 v/v). *N*-Phenyltoluene-*p*-sulphinamide (**1a**), m.p. 123—124 °C, was characterized by comparison with a sample of the corresponding optically active sulphinamide. Allylation of the racemic sulphinamide as before gave compound (**3a**) (83%), m.p. 60—64 °C.

Synthesis of Racemic Sulphinamides (**1c**), (**3c**), (**1b**), (**2b**), *and* (**4b**).—Butyl-lithium in hexane was added with stirring to an equivalent amount of the appropriate amine in THF at −30 °C, under nitrogen. After 15 min, the mixture was kept at −70 °C, and (±)-ethyl toluene-*p*-sulphinate[9] (1 mmol) was added. After an appropriate interval, the mixture was quenched with saturated aqueous ammonium chloride. The aqueous phase was extracted with dichloromethane and the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure to give the crude product. This was purified, in the case of compound (**2b**), by flash chromatography (in diethyl ether–light petroleum, 8:2 v/v). For compounds (**1b**) and (**1c**) the crude products were pure by t.l.c. The compounds were characterized by comparison with the samples of the corresponding optically active sulphinamides. Alkylation of sulphinamides (**1b**) and (**1c**) in the usual way gave compounds (**4b**) and (**3c**) (8%) and (64%) respectively.

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