Reaction between *N,N*-Dialkylhydroxylamines and Sulphinyl Chlorides

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The reactions of several *N,N*-dialkylhydroxylamines with methane- and benzene-sulphinyl chlorides below 0 °C give *O*-sulphinylated intermediates. These rearrange at ambient temperatures to give the corresponding sulphonamides and in some cases the imines and products derived from the decomposition of the accompanying sulphinic acids. N.m.r. spectra (^{1}H and ^{13}C) show strong polarizations in the sulphonamides, indicating a radical-cage mechanism. No CIDNP signals were observed in the imines, which can be formed in a six-electron symmetry-allowed cyclic elimination.

The reactions of hydroxylamine and its *N*-substituted derivatives with sulphinyl chlorides to give sulphonamides have been known for some time.[1] These reactions are rapid at room temperature, and can be carried out under similar conditions irrespective of the extent of substitution in the amino group and the nature of the sulphinyl chloride. No intermediates have so far been detected, but since *O*-methyl-*N*-alkylhydroxylamines given *N*-sulphinylated derivatives under the same conditions,[2] the reaction is assumed to proceed by the attack of nitrogen on the sulphinyl chloride, followed by a rapid rearrangement [equation (1)]. No polarization of the ^{1}H n.m.r. spectrum was

$$\mathrm{RNHOH + R'SOCl \longrightarrow R'S(O)NROH \longrightarrow R'SO_2NHR} \quad (1)$$

observed during the reactions of 1,1-dimethylethanesulphinyl chloride with *N*-substituted hydroxylamines[3] carried out under CIDNP conditions, and there is no evidence, at least in the case of monosubstituted hydroxylamines, for a radical mechanism.

However, it has been shown more recently that oximes,[4] *N*-hydroxycarbamates,[5] and *N*-phenylbenzohydroxamic acid[6] react through *O*-sulphinylated intermediates, which in the case of oximes could be isolated. These undergo homolytic N–O bond cleavage, followed by rearrangement in the radical pair with the formation of an N–S bond, *e.g.* equation (2). This type

$$\mathrm{R^1R^2C{=}NOH + R^3SOCl \xrightarrow{-30\ ^\circ C} R^1R^2C{=}NOS(O)R^3 \xrightarrow{25\ ^\circ C} R^1R^2C{=}NSO_2R^3} \quad (2)$$

of reaction has been observed with a variety of acid chlorides such as thiocarbamoyl chlorides,[7] chlorophosphines,[8] and chlorophosphites,[8] and also between hydroxamic acids and thiocarbamoyl chlorides.[9] Evidence for a radical pathway has been produced from ^{1}H and ^{13}C CIDNP, e.s.r., and kinetic studies.[4–9]

In view of the strong evidence for a radical-cage mechanism in these systems, and the uncertainty over the mechanism of the reactions of *N*-alkylhydroxylamines, we have studied the reactions between *N,N*-disubstituted hydroxylamines and sulphinyl chlorides. This paper presents evidence for the formation of *O*-sulphinylated intermediates which rearrange to mixtures of products including the sulphonamides, at least in part by a radical-pair process.

Results and Discussion

N,N-Disubstituted hydroxylamines are readily *O*-sulphinylated by sulphinyl chlorides in the presence of a molar equivalent of triethylamine or pyridine in dichloromethane at −70 °C. These intermediates (**1a**—**f**), which could be isolated in the solid state below 0 °C, but which generally decomposed above this temperature, were characterized by n.m.r. and i.r. spectroscopy [Table 1 and equation (3)].

$$\mathrm{R^1R^2NOH + R^3SOCl \xrightarrow{-70\ ^\circ C} R^1R^2NOS(O)R^3}\ \textbf{(1)}$$
$$\mathrm{R^1R^2NOS(O)R^3 \xrightarrow{20\ ^\circ C} R^1R^2NSO_2R^3} \quad (3)$$
(1) **(2)**

	R^1	R^2	R^3
a	Me	Me	Me
b	Me	Me	Ph
c	Et	Et	Me
d	Et	Et	Ph
e	$PhCH_2$	$PhCH_2$	Me
f	$PhCH_2$	$PhCH_2$	Ph

The rearrangement is accompanied by a large upfield shift in the ^{13}C resonance of the α-carbon atom of the amino group (Δδ *ca.* 12 p.p.m.). For example the value of δ *ca.* 52.6 for the α-carbon atom of (**1c** and **d**) is similar to that of the corresponding hydroxylamine, *e.g.* δ 53.9 for *N,N*-diethylhydroxylamine. The α-carbon atoms of the rearranged products (**2c** and **d**) resonance upfield at δ *ca.* 42. Electron-attracting substituents on nitrogen are known to produce upfield shifts[10] on α-carbon atoms. The ^{13}C shifts for methanesulphinyl and methanesulphonyl carbon atoms are also different, the latter being at higher field than the former. This effect is also observed for C-1 of benzenesulphinyl as compared with benzenesulphonyl. The methanesulphinyl ^{1}H resonance was typically *ca.* 0.3 p.p.m. to high field of the corresponding methanesulphonyl resonance; this observation is in accord with those of Hudson[4] and Douglass.[11] The sulphinyl group absorbs at *ca.* 1 130 cm^{-1} in the i.r. spectrum.

The *O*-sulphinylhydroxylamines (**1a**—**f**) rearrange in dichloromethane at ambient temperature to give the sulphonamides (**2a**—**f**) in varying yields (Table 2). The sulphonamides (**2a**—**f**) were also synthesized by the action of methane- or benzene-sulphonyl chloride on the appropriate secondary amine in the presence of base. Treatment of *N,N*-disubstituted hydroxylamines with sulphinyl chlorides at room temperature in the presence of base gave the sulphonamides (**2a**—**f**) directly [equation (4)].

$$\mathrm{R^1R^2NOH + R^3SOCl \xrightarrow{25\ ^\circ C} R^1R^2NSO_2R^3} \quad (4)$$
(2)

The data in Table 2 show that the yield of sulphonamide depends on the nature of the substituent. Replacement of benzenesulphinyl chloride with methanesulphinyl chloride

Table 1. N.m.r. data (^1H and ^{13}C) for *N,N*-dialkyl-*O*-sulphinylhydroxylamines (**1a**—**f**) and *N,N*-dialkylsulphonamides (**2a**—**f**)

	δ_H[a,b]				
Compd.	SCH_3	NCH_3	NCH_2Ph	NCH_2CH_3	NCH_2CH_3
(**1a**)	2.50	2.80			
(**1b**)		2.81			
(**1c**)	2.41			2.77	0.98 (*J* 6 Hz)
(**1d**)				2.73	1.12 (*J* 6 Hz)
(**1e**)	2.23		4.31		
(**1f**)			4.33		
(**2a**)	2.75	2.83			
(**2b**)		2.76			
(**2c**)	2.80			3.20	1.18 (*J* 6 Hz)
(**2d**)				3.26	1.14 (*J* 6 Hz)
(**2e**)	2.76		4.32		
(**2f**)			4.32		

	δ_C[c]							
Compd.	SCH_3	NCH_3	NCH_2Ph	CH_2C_{Ar}	SOC_{Ar}	$SO_2Ph(C_1)$	NCH_2CH_3	NCH_2CH_3
(**1a**)[d]	41.6	49.7; 50.3						
(**1b**)[d]		48.7; 49.2			141.8			
(**1c**)[f]	40.6						52.6	10.9
(**1d**)[f]					141.7		52.7	10.8
(**1e**)[e]	41.6		63.5	139.4				
(**1f**)[e]			62.5; 65.9	132.2	143.5			
(**2a**)[g]	33.2	37.6						
(**2b**)		38.0				135.5		
(**2c**)	38.6						41.8	14.3
(**2d**)						140.3	42.1	14.1
(**2e**)	40.3		50.0	135.6				
(**2f**)			50.5	135.6		141.0		

[a] 100 MHz (continuous wave) ^1H shifts relative to internal Me_4Si. [b] (**1a**—**f**) at 0 °C in $CDCl_3$; (**2a**—**f**) at 25 °C in $CDCl_3$. [c] 50.3 MHz (Fourier transform) ^{13}C shifts relative to internal Me_4Si. [d] At −42 °C in $CDCl_3$. [e] At −20 °C in $CDCl_3$. [f] At 0 °C in $CDCl_3$. [g] (**2a**—**f**) at 25 °C in $CDCl_3$; control experiment with (**2b**) showed no significant effect of temperature on chemical shifts.

Table 2. Yields of sulphonamides (**2a**—**f**) from the rearrangement of *O*-sulphinylhydroxylamines (**1a**—**f**) at 20 °C

Compd.	Isolated yield (%)	B.p. [mmHg]	Lit. value	M.p. (°C)	Lit. value
(**2a**)	70	102—104 [8]	103 [8][a]	49—51	50—51[a]
(**2b**)	63			46—48	47—48[b]
(**2c**)	62	110 [6]	112 [6][c]		
(**2d**)	38			42—44	42—43[b]
(**2e**)	45			84—85	
(**2f**)	21			66—67	68[d]

[a] O. Eisleb, Ger. Pat. 735866/1943. [b] A. Ginzberg, *Ber.*, 1903, **36**, 2706. [c] C. S. Marvel, M. D. Helfrick, and J. P. Belsley, *J. Am. Chem. Soc.*, 1929, **51**, 1273. [d] E. Beckmann and E. Fellrath, *Justus Liebig's Ann. Chem.*, 1893, **273**, 23.

increases the yield of sulphonamide. Replacement of *N,N*-dibenzyl with *N,N*-dialkyl has the same effect. Although the changes in yield are appreciable from a preparative point of view, they correspond to relatively small energy changes and are probably due to steric factors depending on the bulk of the substituent.

Product analysis of the rearrangement of (**1f**) showed that the formation of sulphonamide (**2f**) was accompanied by the formation of *N*-benzylidenebenzylamine (**3**) in 27% yield, and presumably benzenesulphinic acid (**4**) produced in an elimination process. Sulphinic acids are known to undergo disproportionation.[12] Our measurements showed 9% of sulphonic acid (**5**), 15% of thiosulphonate (**6**), and water. The water produced causes hydrolysis of part of the imine (**3**) to give *ca.* 6% of benzaldehyde (**7**) (Scheme 1).

Evidence for the involvement of radical intermediates was provided by the observation of CIDNP[13] effects in both ^1H and ^{13}C n.m.r. spectra of the sulphonamides (**2a**, **b**, **e**, and **f**) when the thermolysis of *O*-sulphinylhydroxylamines (**1a**, **b**, **e**, and **f**) was carried out in the probe of an n.m.r. spectrometer. Lawler[14] has pointed out that the observation of strong CIDNP effects in most cases may be taken as good evidence for an important contribution to the overall reaction flux by a radical mechanism. Table 3 shows the results of the CIDNP experiments.

With known g values of <2.0044 for the dialkylaminyl radical[15] and 2.0049 and 2.0045 for methylsulphonyl and phenylsulphonyl radicals,[16] respectively, Kaptein's rules[17] [equation (5)] for the net polarization Γ_{ne} can be applied, where

$$\Gamma_{ne} = \mu\varepsilon\Delta g A_i \quad (5)$$

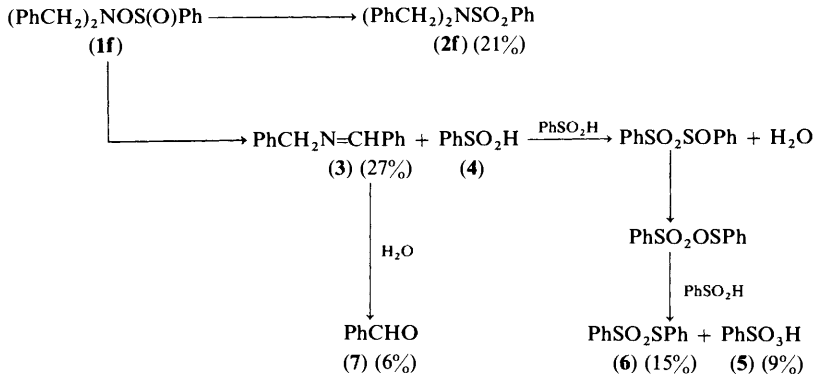
the symbols have their usual significance. For a singlet precursor μ is negative, ε is positive for geminate recombination, Δg is negative for the aminyl moiety and positive for the sulphonyl moiety, and the sign of the hyperfine splitting constant A_i is assumed from the earlier work of Danen.[15,18]

The polarizations predicted from Kaptein's rules (Scheme 2) are in accord with the experimentally observed enhanced absorptions and emissions required for a predominantly radical process with the sulphonamides (**2a**, **b**, **e**, and **f**) arising from geminate recombination [equation (6)]. For example the ^{13}C n.m.r. spectrum during thermolysis of (**1a**) (Figure) shows both methylsulphonyl and *N,N*-dimethyl peaks of the sulphonamide (**2a**) to be in enhanced emission (E). The sign equations (7) and

Table 3. CIDNP Effects in the ^1H and ^{13}C spectra of *N,N*-dialkylsulphonamides produced by the thermolysis of *N,N*-dialkyl-*O*-sulphinylhydroxylamines in $CDCl_3$

Compd.	Ph(C-1)[a]	CH_2(H)	SO_2Me(C)	SO_2Ph(C-1)	NMe(C)	NMe(H)[b]
(**2a**)			E		E	A
(**2b**)				E		A
(**2e**)	A	A	E			
(**2f**)	A	A		E		

[a] Carried out at 61 °C. [b] Carried out at 35 °C. A = enhanced absorption; E = enhanced emission.



Scheme 1. Products of thermolysis of *N,N*-dibenzyl-*O*-phenylsulphinylhydroxylamine

Scheme 2.

$$R^1R^2NOS(O)R^3 \longrightarrow \overline{R^1R^2N\cdot\cdot OS(O)R^3} \longrightarrow R^1R^2NSO_2R^3 \quad (6)$$
(1) (2)

$$^{13}C\ NCH_3\ \Gamma_{ne} = - + - - = - \text{ (emission)} \quad (7)$$

$$^{13}C\ SO_2CH_3\ \Gamma_{ne} = - + + + = - \text{ (emission)} \quad (8)$$

(8) from Kaptein's rules lead to a positive value of ε, as required for cage recombination of a geminate radical pair.

No polarizations were detected in either ^1H or ^{13}C spectra of *N*-benzylidenebenzylamine (**3**) during the thermolysis of (**1e**) and (**1f**). The elimination leading to this imine could proceed by a six-centre six-electron symmetry-allowed process, although a radical-cage process cannot be discounted on the basis of negative CIDNP evidence.

We consider however that the 1,2- rearrangements of *O*-sulphinylated dialkylhydroxylamines do proceed predominantly by a radical-cage process, and this is the first recorded example of a homolytic rearrangement involving an aminyl radical. This is a four-electron process, and it is interesting that all recorded 1,2- and 1,3-rearrangements involving the N–O bond proceed by this mechanism.

Experimental

Starting Materials.—Benzenesulphinyl chloride and methanesulphinyl chloride were prepared by the method of Douglass and Norton.[19] The addition of anyhydrous dichloromethane was found to be beneficial to control the exotherm during the preparation of benzenesulphinyl chloride. Aromatic sulphinyl chlorides may be safely distilled in a Kugelrohr apparatus under high vacuum. *N,N*-Dibenzylhydroxylamine was prepared by the method of Biloski and Ganem.[20] *N,N*-Diethylhydroxylamine and *N,N*-dimethylhydroxylamine hydrochloride were purchased from Aldrich.

N,N-*Dibenzyl*-O-*phenylsulphinylhydroxylamine* (**1f**).—This procedure is typical. An equimolar solution of *N,N*-dibenzylhydroxylamine (1.0 g) and dry triethylamine (0.47 g) in dry dichloromethane (5 ml) cooled to −70 °C was treated with a dichloromethane solution (5 ml) of benzenesulphinyl chloride (0.75 g). The mixture was filtered and the solvent removed by low-temperature (0 °C) evaporation under high vacuum, and *N,N*-dibenzyl-*O*-phenylsulphinylhydroxylamine (**1f**) was obtained as a white crystalline solid (1.57 g, 99%); $\delta_H(CDCl_3)$ 4.33 [s, 4 H, $(CH_2Ph)_2$] and 7.00—7.80 (br, 15 H, aromatic); $\nu_{max.}$(KBr) 1 130 cm^{-1} (S=O).

Table 1 gives ^1H and ^{13}C n.m.r. data for *O*-sulphinyl hydroxylamines (**1a**—**f**) and sulphonamides (**2a**—**f**).

Unambiguous Synthesis of N,N-*Disubstituted Sulphonamides.*—An equimolar solution of dibenzylamine (0.50 g) and triethylamine (0.25 g) in dichloromethane (10 ml) was treated with a dichloromethane solution of methanesulphonyl chloride (0.29 g in 5 ml). The mixture was washed with water (3 × 5 ml), dried ($MgSO_4$), and evaporated under reduced pressure to yield N,N-*dibenzylmethanesulphonamide* (**2e**). The product was recrystallized from cyclohexane (0.59 g, 84%) to give a white solid, m.p. 84—85 °C; $\delta_H(CDCl_3)$ 2.76 (s, 3 H, SO_2CH_3), 4.32 [s, 4 H, $(CH_2Ph)_2$], and 7.24 [s, 10 H, $(CH_2Ph)_2$]; $\delta_C(CDCl_3)$ 40.29, 49.97, 128.07, 128.78, and 135.56; $\nu_{max.}$(KBr) 1 336 and

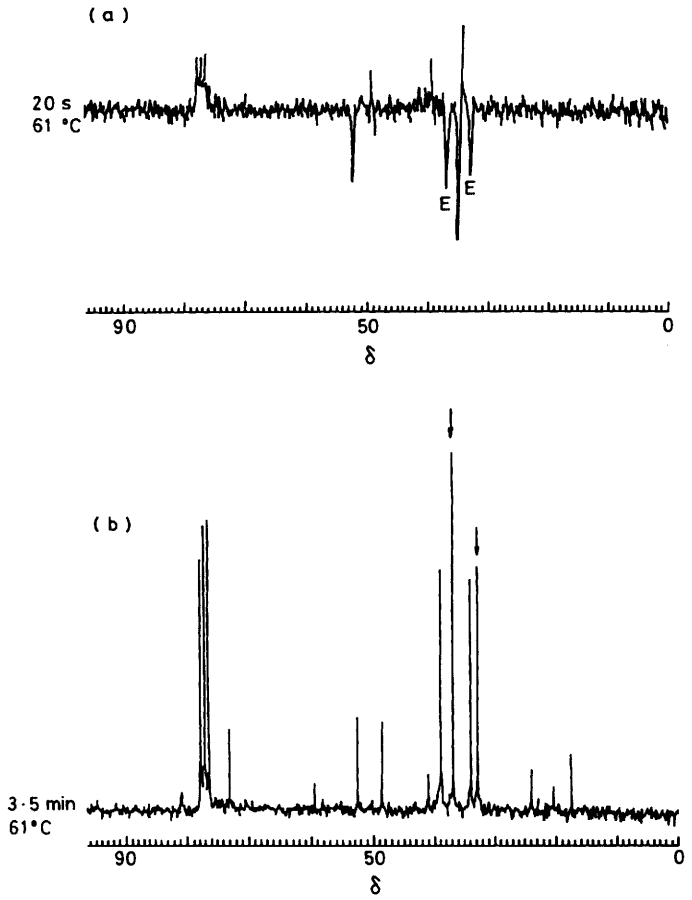


Figure (a) ^{13}C N.m.r. spectrum of the products of thermolysis of *N,N*-dimethyl-*O*-methylsulphinylhydroxylamine (**1a**) (10% w/v in $CDCl_3$) at 61 °C after 20 s. Enhanced emissions (E) at δ 37.6 and 33.2 are due to *N,N*-dimethyl carbon atoms and the methylsulphonyl carbon atom, respectively, of *N,N*-dimethylmethanesulphonamide (**2a**). (b) ^{13}C N.m.r. spectrum after 3.5 min at 61 °C. Arrows indicate unpolarized resonances due to the *N,N*-dimethylmethanesulphonamide (**2a**)

1 150 cm^{-1} (SO_2) (Found: C, 65.4; H, 6.2; N, 5.1. $C_{15}H_{17}NO_2S$ requires C, 65.4; H, 6.2; N, 5.1%). Published methods were used to prepare *N,N*-dimethylmethanesulphonamide (**2a**), *N,N*-dimethylbenzenesulphonamide (**2b**), *N,N*-diethylmethanesulphonamide (**2c**), *N,N*-diethylbenzenesulphonamide (**2d**), and *N,N*-dibenzylbenzenesulphonamide (**2f**) (see footnotes to Table 2).

Product Analysis of Thermal Rearrangement of N,N-*Dibenzyl*-O-*phenylsulphinylhydroxylamine.*—Compound (**1f**) (4.74 g, 1.41 mmol) was dissolved in dichloromethane (30 ml) and the solution was stirred overnight at room temperature. The colourless mixture was evaporated *in vacuo* and the resultant oil was extracted with cold light petroleum (b.p. 30—40 °C). The residue was taken up in dichloromethane and extracted with 2M-sodium hydroxide solution. The solution was neutralized with concentrated hydrochloric acid (phenolphthalein) and warmed to 90 °C; *S*-benzylthiouronium chloride was added and the mixture was set aside overnight. The crystalline product was filtered off and air dried to give the *S*-benzylthiouronium derivative of benzenesulphonic acid (0.9 g), m.p. 148—150 °C (lit.,[21] 150 °C), identical (i.r. spectrum) with an authentic specimen. The dichloromethane fraction was dried ($MgSO_4$) and evaporated and the residue recrystallized from ethanol to yield *N,N*-dibenzylbenzenesulphonamide (**2f**) (1 g, 21%), m.p. 66—67 °C (lit., 68 °C) (footnote *d*, Table 2) as white needles. N.m.r. and i.r. data were consistent with those of an authentic sample.

The light petroleum fractions were combined and evaporated to yield a yellow oil (3.78 g), and distilled in a Kugelrohr apparatus. Two fractions were obtained: (i) b.p. 100 °C at 40 mmHg, shown to be benzaldehyde (0.3 g) by n.m.r. and i.r. spectroscopy and the preparation of the 2,4-dinitrophenylhydrazone derivative (m.p. 178—179 °C; lit.,[22] 179 °C); (ii), b.p. 115 °C at 0.07 mmHg (24 h) demonstrated to be *N*-benzylidenebenzylamine (1.3 g) by comparison of n.m.r. and i.r. data with those of an authentic specimen prepared by the method of Mason and Winder.[23] The residue from the distillation was extracted with light petroleum (b.p. 30—40 °C) and left overnight. A yellow oil separated which was identified by i.r. spectroscopy as *S*-phenylbenzenethiosulphonate (0.7 g). An authentic specimen was prepared by the method of Barnard.[24]

Reaction between Sulphinyl Chlorides and N,N-*Dialkylhydroxylamines.*—This reaction is typical. *N,N*-Dimethylhydroxylamine hydrochloride (1.0 g) and dry pyridine (1.62 g) in dry dichloromethane (10 ml) were cooled to −70 °C and treated dropwise with methanesulphinyl chloride (1.00 g). The mixture was filtered, stirred at room temperature overnight, and then passed down a silica column (15 g SiO_2, Merck, 70—230 mesh) with dichloromethane as eluant.* This yielded *N,N*-dimethylmethanesulphonamide (**2a**) (0.99 g), which was purified by vacuum distillation; b.p. 102—104 °C at 8 mmHg (lit., 103 °C at 8 mmHg) to yield a white solid (0.88 g, 70%), m.p. 49—51 °C (lit., 50—51 °C) (footnote *a*, Table 2).

See Table 2 for physical data of sulphonamides (**2a**—**f**).

CIDNP *Experiments.*—Solutions of (**1a**, **b**, **e**, and **f**) (10 w/v in $CDCl_3$) were prepared at −70 °C and each was filtered into a precooled 10 mm n.m.r. tube. The tube was placed immediately into the probe (at 61 °C) of a Bruker WM 200 SWB spectrometer operating at 50.3 MHz. The ^{13}C spectra were recorded in the pulsed Fourier transform mode. About 15 s elapsed while 75 transients were accumulated (*ca.* 5 μs pulse, 22.5° flip angle, 0.7 s repetition rate, 12.5 kHz spectral width, 16 K data points). The accumulated FID was stored and the free induction decay experiment was repeated. The analogous unpolarized spectrum was obtained after 3.5 min.

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* *N,N*-Diethylbenzenesulphonamide (**2d**) was passed down an alumina column (Merck, 70—230 mesh) with dichloromethane as eluant.

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