Thermal Cycloaddition Reactions of Thiocarbonyl Compounds. Part 3.¹ A Novel [4+2] Cycloaddition Reaction of Thiocarbonyl Compounds with *o*-Quinone Methanides

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Thermal cycloaddition reactions of adamantanethione (3) and thiobenzophenone (8a) with *o*-quinone methanides such as the *o*-benzoquinone methanides (2a—g) and *o*-naphthoquinone methanides (2h—j) occurred smoothly at 180—200 °C to afford, regioselectively, the adamantane-2-spiro-2'-[1,3]benzoxathiines (4a—g), the naphth[1,3]oxathiines (4h—j), and the 2,2-diphenyl-1,3-benzoxathiines (9a) and (9g), all novel [4+2] cycloadducts, in good yields.

The use of thiocarbonyl compounds as components for cycloaddition in organic synthesis has developed quite rapidly in recent years.²⁻⁴ However, they have not been utilized as heterodienophiles even though this would be synthetically useful. In the preceding paper,5 we reported that the cycloaddition of adamantanethione (3), a stable alicyclic thiocarbonyl compound, with α , β -unsaturated carbonyl compounds such as acrolein and methyl vinyl ketone gives adamantane-2-spiro-2'-1'-oxa-3'-thiacyclohex-5'-enes, novel [4 + 2] cycloadducts. We describe here the thermal cycloaddition reactions of compound (3) with o-quinone methanides as the reactive heterodienes;⁶ these provide a facile route to some novel adamantane-2-spiro-2'-[1,3]benzoxathiine ring systems.

Results and Discussion

o-Quinone methanides are known to be very reactive and unstable intermediates, and their dimerization allows easy access to the chroman ring systems.^{24,7} Although there are many reports of o-quinone methanides as a heterodiene component, its reactions with thiocarbonyl compounds have not been investigated. These reactive heterodienes are easily obtained by dehydration of the o-hydroxybenzyl alcohols (1a-f) (Scheme 1, route A) or pyrolysis of the amine (1g) (route B).⁸

When a mixture of adamantanethione (3),⁹ an excess (1.4 times) of salicyl alcohol (1a), and a small amount of hydroquinone as a polymerization inhibitor in dry xylene was heated at 180 °C, the characteristic orange colour of compound (3) disappeared completely after 6 h. A single crystalline cycloadduct (4a) (90%) was isolated together with a small amount of the thione dimer $(6)^9$ (1%) after chromatography on a silica gel column (Scheme 1, Table 1). The structure of compound (4a) was shown to be adamantane-2-spiro-2'-[1,3]benzoxathiine on the basis of the elemental analysis and spectral data (Table 2). In the mass spectrum, the molecular ion peak at m/z 272 (30%) and ion peaks at m/z 239 (9.3%, M^+ -SH) and 166 (100%, adamantanethione) supported the structure (4a) rather than the isomer (5a), as did the appearance of a characteristic singlet in the ¹H n.m.r. spectrum at δ 3.82 (2 H, 4-H) and ¹³C n.m.r. signals at δ 156.2 (s, C-8a), 119.3 (s, C-4a), and 88.7 p.p.m. (s, C-2). In addition, catalytic hydrogenation of compound (4a) with Raney Ni (W-4 type) in ethanol afforded 2-ethoxy-2-(omethylphenoxy)adamantane (7a) (88%) (Scheme 1), as a result of the initial ethanolysis of the C(2)-S bond followed by hydrogenolysis of the C-SH bond.

The cycloaddition of compound (3) to other substituted obenzoquinone methanides (2b—f), generated in situ by dehydration of the corresponding substituted salicyl alcohols (1b—f), occurred similarly on heating at 180—200 °C in xylene to afford the corresponding 1,3-benzoxathiine derivatives (4b f) (51—89% yields) (Table 1). On the other hand, the reaction of compound (3) with the o-quinone methanide (2g), generated by pyrolysis of the amine (1g) at 180 °C for 3 h in xylene, also afforded a cycloadduct (4g) (63%) and the thione dimer (6) (1%). The given structures (4b—g) are supported by analytical and spectral data (Table 2).

Table	1.	Reaction	of	the	thiones	(3)	and	(8a)	with	o-quinone	methanides	(2a—j)	

Thione	o-Quinone methanide	Method "	Temp. (°C)	Time (h)	Product [Yield (%)] ^b
(3)	(2a)	Α	180	6	(4a)[90], (6)[1]
(3)	(2b)	Α	180	4	(4b)[55], (6)[3]
(3)	(2c)	Α	180	4	(4c)[70], (6)[3]
(3)	(2d)	Α	180	6	(4d)[52], (6)[5]
(3)	(2e)	Α	180	20	(4e)[89], (6)[3]
(3)	(2f)	Α	200	30	(41)[51], (6)[8]
(3)	(2g)	В	180	3	(4g)[63], (6)[2]
(3)	(2h)	Α	180	20	(4h)[82], (6)[10]
(3)	(2h)	В	180	5	(4h)[88]
(3)	(2i)	Α	180	15	(41)[40], (6)[9]
(3)	(2j)	Α	180	20	(4j)[40], (6)[9]
(8a)	(2a)	Α	180	20	(9a)[79]
(8a)	(2g)	В	140	96	(9 g)[45]

" All reactions were carried out in dry xylene and in the presence of hydroquinone (5 mol % to thione) as a polymerization inhibitor. A = dehydration of *o*-hydroxymethylphenol or naphthol; B = pyrolysis of amine. ^b Isolated yields after chromatography on a silica gel column.

Elemental analysis (%)

Molecular

Compound			m/z (%)	formula	Foun	d (requi	red)
(M n °C)	v ^b /cm ⁻¹	δ. /p.p.m.'			C	H	Ň
(111)	2 0 50 2 000 2 945 1 579	7.20 + 6.90 (4.11 m)	272 (20) 4 220 (0 2)		74 0	74	
(48)	3 050, 2 900, 2 845, 1 578,	$7.50-0.60$ (4 Π , III),	272(30), 239(9.3), 133(27)	$C_{17} M_{20} OS$	(74.5	(7 44)	
(68.069.0)	1 485, 1 450, 1 305, 1 230,	3.82 (2 Pl, s),	107 (45), 100 (100), 155 (57), 104 (25), 107 (20), 01 (67)		(/4.90)	(7.44)	
(4 •)	1 100, 1 050, 1 002, 755	2.55 - 1.40 (14 H, m)	124(35), 107(20), 91(07)		75 4	70	
(4b)	3 040, 3 010, 2 910, 1 622,	7.10—0.50 (3 H, m),	280(44),"233(33),	$C_{18} \Pi_{22} OS$	13.4	1.0	
(77.078.0)	1 578, 1 505, 1 315, 1 155,	3.75 (2 H, s), 2.28 (s, 3 H),	203(11), 100(100), 150(15),		(75.46)	(7.74)	
	1 130, 1 052, 1 022, 800	2.50-1.40 (14 H, m)	132 (18), 91 (33), 77 (20)	0 11 00	757	70	
(4c)	3 050, 3 020, 2 895, 2 845,	7.15 - 6.60 (3 H, m),	280(33), 233(31),	$C_{18} H_{22} US$	13.1	1.0	
(96.0-97.0)	1 595, 1 465, 1 450, 1 220,	3.82 (2 H, s), 2.28 (s, 3 H),	107(22), 100(100), 151(7.8),		(75.48)	(7.74)	
	1 105, 1 080, 1 010, 770	2.50—1.45 (14 H, m)	133 (10), 91 (25)	o occi			
(4d)	2 900, 2 845, 1 575, 1 480,	7.18-6.70 (3 H, m),	306 (28)," 308 (13),	$C_{17}H_{19}OSCI$	66.5	6.3	
(oil)	1 275, 1 230, 1 122, 1 102,	3.74 (2 H, s),	256 (33), 166 (100), 155 (33),		(66.54)	(6.24)	
	1 050, 1 005, 910, 830	2.50—1.30 (14 H, m)	150 (81), 133 (19), 86 (92)				
(4e)	3 080, 2 900, 2 845, 1 612,	8.20—7.90 (2 H, m),	317 (22)," 284 (4.0),	$C_{17}H_{19}NO_3S$	66.2	6.1	4.45
(170-171)	1 578, 1 510, 1 485, 1 340,	7.206.90 (1 H, m),	166 (100), 133 (14), 124 (12),		(66.33)	(6.03)	(4.41)
	1 248, 1 095, 990, 750	3.88 (2 H, s),	121 (18), 91 (18), 79 (10)				
		2.52—1.40 (14 H, m)					
(4f)	3 050, 3 020, 2 900, 2 845	6.90-6.50 (3 H, m),	302 (55), ^d 269 (33),	$C_{18}H_{22}O_{2}S$	71.5	7.3	
(138-139)	1 580, 1 475, 1 260, 1 218,	3.83 (3 H, s), 3.82 (2 H, s),	166 (39), 136 (100), 135 (27),		(71.49)	(7.33)	
	1 090, 1 005, 768, 735	2.60—1.40 (14 H, m)	107 (18), 91 (24)				
(4 g)	2 890, 2 840, 1 475, 1 440,	6.72 (1 H, br s),	300 (75), ⁴ 267 (58),	$C_{19}H_{24}OS$	76.1	7.9	
(100-102)	1 212, 1 150, 1 100, 1 055,	6.60 (1 H, br s), 3.68 (2 H, s),	183 (13), 166 (100), 150 (16),		(75.95)	(8.05)	
	1 005, 900, 850, 720	2.60—1.40 (20 H, m)	134 (54), 105 (21), 91 (46)				
(4h)	3 040, 2 930, 1 620, 1 595,	7.957.05 (6 H, m),	322 (24), ⁴ 290 (12),	$C_{21}H_{22}OS$	78.3	6.9	
(137-138)	1 465, 1 448, 1 232, 1 220,	4.12 (2 H, s),	289 (16), 166 (100), 156 (5.0),		(78.22)	(6.88)	
	1 005, 908, 808, 748	2.60—1.30 (14 H, m)	91 (24), 86 (34), 84 (55)				
(4i)	3 045, 2 895, 2 845, 1 630,	8.45-8.15 (1 H, m),	322 (85), ^d 290 (20),	C21H22OS	78.2	6.9	
(209-210)	1 600, 1 570, 1 390, 1 375,	7.90-7.70 (5 H, m),	289 (56), 166 (11), 156 (100),		(78.22)	(6.88)	
. ,	1 200, 1 095, 1 000, 800	3.29 (2 H, s),	128 (85), 119 (12), 91 (22)				
		2.70-1.20 (14 H, m)					
(4i)	3 045, 2 900, 2 830, 1 635,	7.907.20 (6 H, m),	322 (32), ^d 290 (11),	C,,H,,OS	78.2	6.9	
(153-154)	1 605, 1 450, 1 248, 1 160,	4.00 (2 H, s),	289 (21), 166 (100), 156 (21),	21 24	(78.22)	(6.88)	
(, , , ,	1 105, 1 000, 905, 762	2.70-1.20 (14 H, m)	133 (21), 128 (21), 91 (26)		. ,	. ,	
(9a)	3 050, 3 020, 1 575, 1 485,	7.80-6.80 (14 H, m).	304 (39), ⁴ 199 (13),	C ₂₀ H ₁₆ OS	78.9	5.3	
(119 - 120)	1 445, 1 306, 1 218, 1 165,	3.58 (2 H. s)	198 (100), 197 (13), 166 (17),	- 2010	(78.91)	(5.30)	
()	1 040, 998, 748, 700		165 (96), 121 (49), 77 (22)		()	(/	
(9 g)	3 060, 3 025, 2 920, 1 598.	7.85 (10 H. m), 6.08 (1 H. br s).	332 (37).4 199 (20).	C ₂₂ H ₂₀ OS	79.5	6.0	
(113-114)	1 478 1 445 1 215 1 155	6.87 (1 H, br s), 3.56 (2 H, s).	166 (20), 165 (85), 134 (15),	- 1220-50	(79.48)	(6.06)	
(1 012 870 752 700	2.40 (3 H, s) 2.16 (3 H, s)	121 (44), 91 (17), 77 (17)		(,,,,,,,))	(0.00)	
	1012, 070, 792, 700						

Table 2. Physical and analytical data of the cycloadducts (4a-j) and (9a) and (9g)

^{*a*} Purified on a silica gel column. ^{*b*} Solid compounds were scanned in KBr disks and oils were scanned as neat films. ^{*c*} All ¹H n.m.r. spectra were measured in CDCl₃. ^{*d*} M^+ Ion peaks.

The cycloaddition of compound (3) to the o-naphthoquinone methanides (1h-j) generated by either method. A or B (Table 1) occurred similarly, as shown in Scheme 1; the reaction of (3) with 1-hydroxymethyl-2-naphthol (1h) in xylene at 180 °C for 20 h afforded the cycloadduct (4h) (82%) and the thione dimer (6) (10%) after chromatography. The adduct (4h) was characterized as adamantane-2-spiro-2'-naphth[2,1-e][1,3]oxathiine, based on the elemental analysis and spectral data (Table 2). Characteristic ¹H n.m.r. signals at δ 7.95–7.05 (m, Ar), 4.12 (s, 4'-H), and 2.70-1.20 (m, Ad) in the ratio 3:1:7 were compatible with structure (4h). When the amine $(1k)^{10}$ was pyrolysed with compound (3) under the same conditions, the same product (4h) was obtained alone in 88% yield. However, the reaction of compound (3) with the o-naphthoquinone methanides (2i) and (2j), from the o-hydroxymethylnaphthols (1i) and (1j), gave regioisomers of (4h) such as naphth[1,2-e]-(4i) and naphth[2,3-e]-[1,3]oxathiine (4j), each in 40% yield. The modest yields of (4i) and (4j) compared with that of (4h) might indicate that the o-naphthoquinone methanides (2i) and (2j) have lower reactivities than (2h).

The reactions of other thiocarbonyl compounds such as thiobenzophenone (8a),¹¹ 4,4'-dimethoxythiobenzophenone (8b), and thioxanthone (8c) with the *o*-quinone methanides (2a) and (2g) were also examined. That of (8a) took place at 140—

180 °C, and the 1,3-benzoxathiines (9a) and (9g) were obtained regioselectively in 79 and 45% yields, respectively (Scheme 1); however, (8b) and (8c) were unreactive towards (2a) and (2g), and even on heating in xylene at 140—180 °C for 1 week, no cycloadducts were obtained, the thiones (8b) and (8c) gradually decomposing under the reaction conditions. The thione (8a) had not undergone cycloaddition with the *o*-naphthoquinone methanides (2h—j) after 1 week at 180 °C.

The observed high regiospecificity in these cycloadditions can be explained in terms of frontier molecular orbital (FMO) interactions.¹² The frontier orbitals of the thione $(3)^{5,13}$ and the *o*-quinone methanide $(2a)^{14}$ based on CNDO/2 calculation are schematically shown in the Figure. The solid arrow indicates the dominant overlap, the interaction of the LUMO of the diene with the HOMO of the dienophile (*i.e.* a LUMO controlled or inverse Diels-Alder type reaction).¹⁵ The large-large (the overlap of C-7 with S)/small-small (O with C-2) interaction should be the most favourable,¹² thus predicting the experimentally observed regioselectivity to afford the product (4a).

The above [4 + 2] cycloadditions of compounds (3) and (8a) with the *o*-quinone methanides (2a-j) thus provides a facile route to the hitherto unknown 1,3-benzoxathiine and naphth-[1,3] oxathiine ring systems.



Scheme. Reagents: i, (8); ii, Raney Ni, EtOH



(4		(\mathbf{J})						
номо	LUMO	номо	LUMO					
C(7) -0.437	C(7) 0.505	C(2) - 0.397	C(2) - 0.588					
C(6) -0.250	C(6) -0.217	S -0.658	S 0.661					
C(5) 0.378	C(5) - 0.348							
C(4) 0.385	C(4) 0.297							
C(3) - 0.273	C(3) 0.364							
C(2) - 0.390	C(2) - 0.322							
C(1) 0.108	C(1) - 0.295							
O 0.466	O 0.407							

Figure. Frontier orbital coefficients and energies (CNDO/2)

Experimental

M.p.s were taken in a sealed tube on a Yanagimoto micromelting point apparatus and are uncorrected. Microanalyses were performed with a Perkin-Elmer 240B elemental analyser. I.r. spectra were recorded on a JASCO A-100 spectrometer. ¹H and ¹³C N.m.r. spectra were taken at 25 °C with a JEOL JMN-C-60HL instrument at 60 MHz and a JEOL-FX-60FT spectrometer at 15.04 MHz, respectively, using Me₄Si as an internal standard in CDCl₃. Mass spectra were obtained with a JEOL JMS-D10 mass spectrometer at 75 eV. G.l.c. analyses were carried out by using a JEOL JGC-20K gas chromatograph on 1-or 2-m Silicone SE-30 column at 100–200 °C.

Materials.—Adamantanethione (3),⁹ thiobenzophenone (8a),¹¹ 4,4'-dimethoxythiobenzophenone (8b),¹¹ and thioxanthone (8c)¹¹ were prepared by the reported method and purified on a silica gel (Kieselgel 60, 70—230 mesh) column by elution with n-hexane. The amines (1g)^{8a} and (1k)¹⁰ were prepared according to the procedures in the literature. The substituted salicyl alcohols (1b—f) and o-hydroxymethylnaphthols (1h—j) were prepared according to the standard procedures by the reduction of the corresponding carboxylic acids or aldehydes. The other reagents were commercial materials. All the solvents were carefully dried and distilled before use.

Calculations.—The calculations were carried out on a FACOM M-200 computer at Nagoya University Computation Centre. The geometry of o-quinone methanide (2a) required for the CNDO/2 calculation¹⁶ was estimated from an assumed structure made up with the standard bond length and angles.

Adamantane-2-spiro-2'-[1,3]benzoxathiine (4a).---A mixture of compound (3) (166 mg, 1.00 mmol), salicyl alcohol (1a) (173 mg, 1.40 mmol), and hydroquinone (5 mg, 0.05 mmol) in dry xylene (4 ml) was heated at 180 °C in a sealed tube (12 mm diameter \times 260 mm length) for 6 h under argon. The orange colour of the solution gradually faded during this time to give a colourless solution. After removal of the solvent under reduced pressure, the resulting residue was chromatographed on a silica gel column by elution with n-hexane-benzene (8:1 v/v). The first fractions gave the dimer (6)⁹ of (3) (2 mg, 1%), m.p. > 300 °C. The second fractions gave the cycloadduct (4a) (243 mg 90%) as a white precipitate. An analytical sample was obtained after recrystallization from n-hexane-CHCl₃ (5:1 v/v). δ_{c} (CDCl₃) 152.6 (s, 1 C), 128.6 (d, 1 C), 127.9 (d, 1 C), 120.4 (d, 1 C), 119.3 (d, 1 C), 119.3 (s, 1 C), 88.7 (s, 1 C), 37.9 (t, 1 C), 36.0 (d, 2 C), 34.3 (t, 2 C), 32.7 (t, 2 C), 27.3 (d, 1 C), 27.0 (d, 1 C), and 24.4 p.p.m. (t, 1 C); for other physical data, see Table 2.

6,8'-Dimethyl-adamantane-2-spiro-2'-[1,3]benzoxathiine

(4g).—A mixture of compound (3) (120 mg, 0.72 mmol), 2,4dimethyl-6-dimethylaminomethylphenol (1g)^{8a} (155 mg, 0.87 mmol), and hydroquinone (4 mg, 0.36 mmol) in xylene (4 ml) was heated at 180 °C for 3 h as above. Evaporation of the solvent under reduced pressure and chromatography on a silica gel column (n-hexane-benzene 9:1 v/v) gave the *thione dimer* (6) (2 mg, 2%) and the cycloadduct (4g) (136 mg, 63%), in order of elution. For physical data, see Table 2.

Adamantane-2-spiro-2'-naphth[2,1-e][1,3]oxathiine (4h).---

(a) From o-hydroxymethylnaphthol. A mixture of compound (3) (100 mg, 0.60 mmol), 1-hydroxymethyl-2-naphthol (1h) (150 mg, 0.86 mmol), and hydroquinone (3 mg, 0.03 mmol) in xylene (4 ml) was heated in a sealed tube at 180 °C for 20 h. Chromatography of the reaction mixture on a silica gel column using n-hexane-benzene gave the dimer (6) (8 mg, 10%), unchanged compound (3) (20 mg), and the adduct (4h) (128 mg, 82%), in order of elution. An analytical sample of compound (4h) was obtained after recrystallization from n-hexane-dichloromethane. For physical data, see Table 2.

(b) From amine. A solution of compound (3) (100 mg, 0.60 mmol), 1-dimethylaminomethyl-2-naphthol (1k)¹⁰ (158 mg, 0.79 mmol), and hydroquinone (3 mg, 0.03 mmol) in xylene (4 ml) was heated at 180 °C for 5 h. The reaction mixture was subjected to silica gel chromatography and fractional crystallization from n-hexane-dichloromethane gave the adduct (4h) as colourless crystals (170 mg, 88%).

Adamantane-2-spiro-2'-naphth[1,2-e][1,3]oxathiine (4i).—A mixture of compound (3) (100 mg, 0.66 mmol), 2-hydroxymethyl-1-naphthol (1i) (150 mg, 0.86 mmol), and hydroquinone (3 mg, 0.03 mmol) in xylene (4 ml) was heated at 180 °C for 15 h. Similar work-up followed by chromatography on a silica gel with n-hexane-benzene gave the dimer (6) (10 mg, 9%) and compound (4i) (86 mg, 40%) in order of elution.

Adamantane-2-spiro-2'-naphth[2,3-e][1,3]oxathiine (4j).—A mixture of compound (3) (100 mg, 0.60 mmol), 3-hydroxymethyl-2-naphthol (1j) (150 mg, 0.86 mmol), and hydroquinone (3 mg, 0.03 mmol) in xylene (4 ml) was heated at 180 °C for 20 h. Chromatography of the reaction mixture on a silica gel column (n-hexane-benzene) gave the dimer (6) (7 mg, 9%), unchanged compound (3) (25 mg), and compound (4j) (58 mg, 40%), in order of elution. For physical data, see Table 2.

Reduction of Compound (4a) with Raney Ni.—A mixture of (4a) (70 mg, 0.26 mmol) and Raney Ni (W-4 type, ca. 1 ml) in ethanol (3 ml) was stirred at room temperature for 24 h under hydrogen. After filtration of the catalyst through Celite 545 and

washing with ethanol, the combined filtrate and washings were evaporated under reduced pressure to afford practically pure 2ethoxy-2-(o-methylphenoxy)adamantane (7a) as a colourless oil (65 mg, 88%) (Found: C, 79.9; H, 9.1. $C_{19}H_{26}O_2$ requires C, 79.68; H, 9.15%); v_{max} (film) 3 025, 2 940, 2 860, 1 603, 1 495, 1 235, 1 190, 1 120, 1 110, 1 050, 1 000, 935, and 760 cm⁻¹; δ_H (CDCl₃) 7.60—6.50 (4 H, m), 3.80 (2 Hq, J 7.5 Hz,), 2.24 (3 H, s), 1.22 (3 H, t, J 7.5 Hz), and 2.60—1.20 (m, 14); m/z 286 (M⁺, 1.0%), 242 (7.0), 241 (M⁺ – OEt, 7.0), 179 (M⁺ – OAr, 100), 151 (64), and 134 (77).

Compound (7a) was easily decomposed to adamantanone and *o*-cresol by chromatography on a silica gel or alumina column (g.l.c. and i.r. analyses).

2,2-Diphenyl-1,3-benzoxathiine (9a).—A solution of thiobenzophenone (8a) (140 mg, 0.70 mmol) salicyl alcohol (1a) (150 mg, 1.20 mmol), and hydroquinone (4 mg, 0.36 mmol) in dry xylene (4 ml) was heated in a sealed tube at 180 °C for 20 h under argon. The solvent was removed under reduced pressure and chromatography on a silica gel column with n-hexanebenzene (9:1 v/v) followed by recrystallization from n-hexane gave adduct (9a) as white crystals. For physical data, see Table 2.

6,8-Dimethyl-2,2-diphenyl-1,3-benzoxathiine (9g).—A mixture of the thione (8a) (198 mg, 1.00 mmol), the amine (1g)^{8a} (200 mg, 1.12 mmol), and hydroquinone (5 mg, 0.05 mmol) in dry xylene (4 ml) was heated in a sealed tube at 140 °C for 96 h. After removal of the solvent, the remaining oil was chromatographed on a silica gel column eluting with n-hexane-benzene (8:1 v/v) to afford compound (9g) (145 mg, 45%) as a white precipitate. An analytical sample was obtained after recrystallization from n-hexane. For physical data, see Table 2.

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