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HOTf-Catalyzed Rearrangement of Methylenecyclopropane Aryl and Alkyl Alcohols

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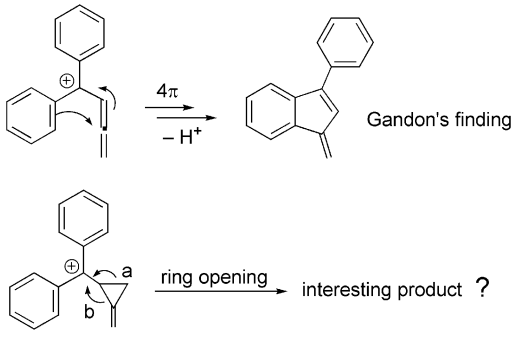
An efficient method to synthesize multisubstituted naphthalene and cyclobutanol derivatives through ring opening/ring enlargement of readily available methylenecyclopropane diaryl alcohols or dialkyl- and monoalkyl- as well as monoaryl alcohols in moderate to good yields has been described in this paper. The formation of naphthalene derivatives is a sequential reaction involving a cation-induced ring opening of cyclopropane, a Friedel–Crafts alkylation reaction, followed by aromatization. On the other hand, the production of cyclobutanol derivatives is a cation-induced ring-enlargement process. The scope and limitations have also been presented.

Introduction

Methylenecyclopropanes (MCPs) are generally utilized as building blocks in organic synthesis for their ready accessibility as well as diverse reactivity driven by the relief of ring strain.[1] The ring-opening reactions of MCPs are synthetically useful protocols in the construction of complex product structures that have been studied extensively thus far.[2] For example, during the last 10 years, Lewis/Brønsted acids and transition-metal-catalyzed reactions involving ring opening of MCPs to form a variety of novel carbocycles and heterocycles have been extensively investigated.[3,4] Previously, we reported a very interesting silver- and gold-catalyzed rearrangement of propargylic alcohols tethered with MCPs for the stereoselective synthesis of allenylcyclobutanols and 1-vinyl-3-oxabicyclo[3.2.1]octan-8-one derivatives in moderate to good yields under mild conditions.[5] Such a transformation involves a cation-induced ring-opening rearrangement of cyclopropane to produce an oxygen-atom-containing heterocyclic ring. Moreover, recently, Gandon and co-workers disclosed a general method for the preparation of benzofulvenes from diaryl α-hydroxyallenes through Nazarov-type cyclizations in the presence of silver and Brønsted acids (Scheme 1).[6] On the basis of these findings, we envisaged that an adjacent in situ formed similar cationic intermediate might induce ring-opening rearrangement of the cyclopropane to give interesting products (Scheme 1). Therefore, we synthesized a variety of MCP aryl alcohols or alkyl alcohols to examine such a rearrangement. During our ongoing investigation on the reaction outcome of MCP diaryl alcohols **1** or dialkyl- and monoalkyl- as well as monoaryl alcohols **3** using a variety of Lewis acids or Brønsted acids, to our delight, it was found that a set of multisubstituted naphthalenes **2** and cyclobutanols **4** could be obtained in moderate to good yields rather than benzofulvenes. Herein, we wish to report the full details of this novel ring-opening/ring-expansion rearrangement of MCP diaryl alcohols **1** or dialkyl- and monoalkyl- as well as monoaryl alcohols **3** catalyzed by Lewis/Brønsted acid under mild conditions.



Scheme 1. The comparison between allene and MCP.

Results and Discussion

We initially utilized MCP diphenyl alcohol **1a** as the substrate to investigate its reaction outcome in dichloromethane (DCM) at room temperature (20 °C) in the presence of 10 mol-% of Brønsted acid trifluoromethanesulfonic acid (CF_3SO_3H, HOTf; as for the synthesis of **1a**, see the Supporting Information). It was found that treatment of **1a** for 1.0 h delivered the corresponding naphthalene **2a** as a white solid in 75% yield after usual workup and purification by column chromatography on silica gel (Table 1, Entry 1).[7]

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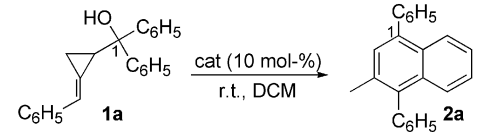
The use of AgOTf and $Yb(OTf)_3$ as the catalysts did not promote this reaction after 24 h, perhaps because both of these two Lewis acids do not have enough acidity to initiate the cationic intermediate in this reaction. We found that $BF_3{\cdot}Et_2O$ performed very well in this reaction, affording **2a** in 50% yield within 10 min (Table 1, Entry 4). Other Lewis acids such as TMSOTf and $Fe(OTf)_2{\cdot}2MeCN$ and the Brønsted acid CF_3CO_2H were also suitable catalysts in this reaction, giving **2a** in 40–69% yields within 1.0–10.0 h (Table 1, Entries 5–8). Conducting the reaction at 0 °C with the use of HOTf and $BF_3{\cdot}Et_2O$ as the catalysts produced the corresponding naphthalene derivative **2a** in 80 and 51% yield, respectively (Table 1, Entries 9 and 10).

Table 1. Optimization of the reaction conditions.



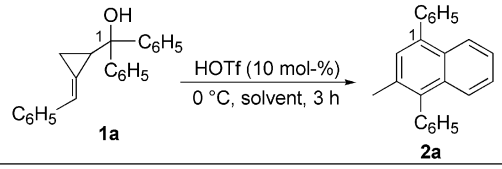
Entry	Catalyst	*t* [h]	Yield [%][a]
			2a
1	HOTf	1	75
2	AgOTf	24	NR
3	$Yb(OTf)_3$	24	NR
4	$BF_3{\cdot}Et_2O$	0.2	50
5	CF_3CO_2H	5	40
6	TMSOTf	5	66
7	$Fe(OTf)_2{\cdot}2CH_3CN$	10	55
8	$FeCl_3$	1	69
9	HOTf	3	80[b]
10	$BF_3{\cdot}Et_2O$	1	51[b]

[a] Isolated yield. [b] The reaction was carried out at 0 °C.

Next, we attempted to investigate the solvent effect of this reaction in the presence of HOTf (10 mol-%) at 0 °C. The results of these experiments are summarized in Table 2. Using 1,2-dichloroethane (DCE) and toluene as the solvents, it was found that **2a** was obtained in 88 and 85% yield within 3 h, respectively (Table 2, Entries 1 and 2). In other oxygen- or nitrogen-atom-containing solvents such as THF or MeCN, the reaction became sluggish, yielding **2a** in 20 and 30% yield under identical conditions, respectively (Table 2, Entries 3 and 4). Moreover, the use of a protogenic solvent such as MeOH in this reaction turned out to be unsuccessful, probably because the H^+ species was completely deactivated by MeOH, as the oxygen atom in MeOH can coordinate to Brønsted acids such as HOTf (Table 2, Entry 5).

Having established these optimized reaction conditions, we next attempted to examine the scope and limitations of this reaction by using a variety of other MCP diaryl alcohols having two identical aromatic groups (R^2) at the C-1 position. The results are outlined in Table 3. As for substrates **1b**, **1d**, and **1f** having electron-donating group substituted aromatic rings (R^1) and **1c**, **1g**, and **1h** bearing electron-withdrawing group substituted aromatic rings (R^1),

Table 2. Solvent effect of the reaction.

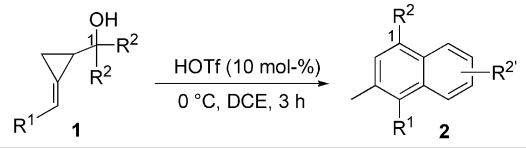


Entry	Solvent	Yield [%][a]
		2a
1	DCE	88
2	toluene	85
3	THF	20
4	CH_3CN	30
5	CH_3OH	NR

[a] Isolated yield.

the corresponding naphthalene derivatives **2b**, **2d**, and **2e** as well as **2c**, **2g**, and **2h** were obtained in 66–86% yield, respectively, suggesting that the electronic properties of the aromatic R^1 groups have little impact on the outcome of the reaction (Table 3, Entries 1, 3, 5 and 2, 7, 8). However, by introducing three strongly electron-donating MeO groups on the benzene ring of R^1 (substrate **1e**), the reaction became disordered and a complex mixture was obtained (Table 3, Entry 4). Notably, the same product **2a** was obtained in 74% yield by using *Z*-**1a** as the substrate under identical conditions (Table 3, Entry 6). On the other hand, in the case of **1i**, in which R^2 is a *para*-methyl-substituted aromatic group, the reaction also proceeded smoothly, giving the corresponding naphthalene derivative **2i** in 87% yield (Table 3, Entry 9). The preparation of aliphatic substrate **1j** ($R^1 = C_7H_{15}$) was not successful. It was found that during the preparation of MCP dialkyl alcohol **1j**, a complex mixture was formed (see the Supporting Information).

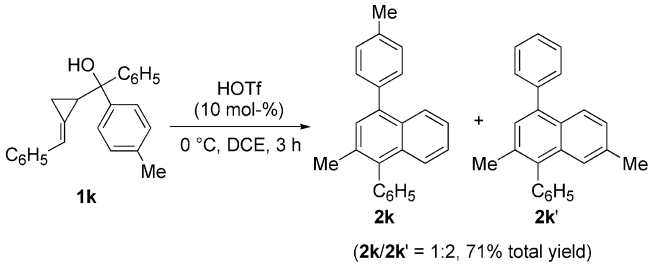
Table 3. HOTf-catalyzed rearrangement of MCP diaryl alcohols having two identical aromatic groups at the C-1 position.



Entry	R^1/R^2	Yield [%][a]
		2
1	**1b**, *p*-MeC_6H_4/C_6H_5	**2b**, 86
2	**1c**, *p*-PhC_6H_4/C_6H_5	**2c**, 79
3	**1d**, *p*-$MeOC_6H_4/C_6H_5$	**2d**, 80
4	**1e**, 3,4,5-$(MeO)_3C_6H_2/C_6H_5$	complex mixture
5	**1f**, *m*-MeC_6H_4/C_6H_5	**2e**, 66
6	*Z*-**1a**/C_6H_5	**2a**, 74
7	**1g**, *p*-BrC_6H_4/C_6H_5	**2g**, 84
8	**1h**, *p*-ClC_6H_4/C_6H_5	**2h**, 79
9	**1i**, C_6H_5/*p*-MeC_6H_4	**2i**, 87
10	**1j**, C_7H_{15}/C_6H_5	**2j**, –[b]

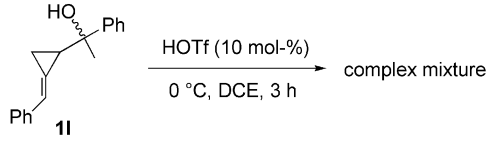
[a] Isolated yield. [b] The preparation of aliphatic substrate **1j** was failed.

In the case of MCP diaryl alcohol **1k** having two different aromatic groups at the C-1 position, the corresponding naphthalene derivative was obtained as a mixture of isomers **2k** and **2k′** (1:2) in 71% total yield under the standard conditions (Scheme 2).



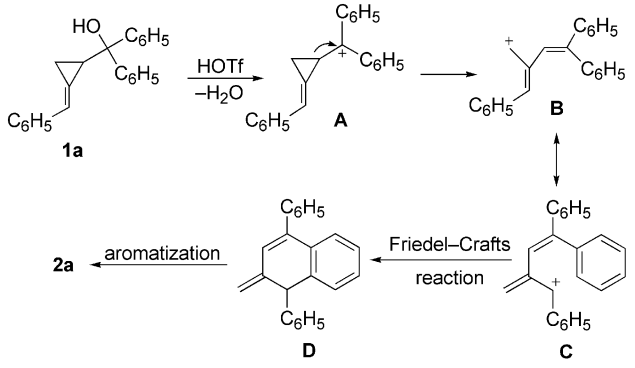
Scheme 2. MCP diaryl alcohol **1k** having two different aromatic groups at the C-1 position.

The two aromatic rings in starting materials **1** are essential in this reaction to produce naphthalene derivatives in good yields because the use of MCP monoaryl alcohol **1l** (a pair of diastereoisomers) as the substrate gave a complex mixture under the standard conditions, presumably because the in situ generated cationic intermediate derived from the MCP monoaryl alcohol is not very stable for the next reaction, such as an intramolecular Friedel–Crafts reaction (see the plausible mechanism, Scheme 3).



Scheme 3. Reaction of MCP monoaryl alcohol **1l** under the standard conditions.

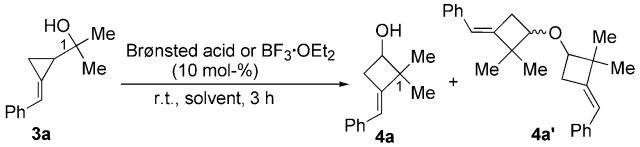
A plausible reaction mechanism for this ring-opening rearrangement is shown in Scheme 4 by using **1a** as a model. The in situ generated cationic intermediate **A** undergoes ring-opening to give intermediate **B**, which produces intermediate **C** through allylic rearrangement. The intramolecular Friedel–Crafts reaction affords intermediate **D**, which undergoes aromatization to give naphthalene **2a**.



Scheme 4. A plausible reaction mechanism.

Interestingly, as for MCP dimethyl alcohol **3a**, the ring enlargement takes place to give the corresponding cyclobutanol derivative **4a** along with ether derivative **4a′** (a pair of diastereoisomers) in 85% total yield rather than the naphthalene derivative under identical conditions (Table 4, Entry 1). To obtain cyclobutanol derivative **4a** as a sole product, we subsequently optimized the reaction conditions, and the results of these experiments are summarized in Table 4. It was found that a similar result was obtained if $BF_3{\cdot}OEt_2$ (10 mol-%) was used as the catalyst (Table 4, Entry 2), and the Brønsted acid TFA (CF_3CO_2H) afforded **4a** and **4a′** in 53% total yield (Table 4, Entry 3). Adding H_2O (2.0 equiv.) to the reaction mixture did not suppress the formation of **4a′**, giving **4a** and **4a′** in 86% total yield with a ratio of 1.4:1 (Table 4, Entry 5). Examination of solvent effects revealed that **4a** could be obtained as the major product (**4a**/**4a′** = 6:1) if $MeNO_2$ was used as the solvent in the presence of HOTf (Table 4, Entry 6). We carried out the reaction at a lower concentration of $MeNO_2$ (0.05 M, and it was found that the yield of **4a** was 70%, which is almost same as that obtained at a concentration of 0.1 M (Table 4, Entry 6). Under these optimized conditions, the substrate scope was also examined, and the results are outlined in Table 5. The corresponding cyclobutanols **4a**–**l** were obtained in 38–72% yield along with trace amounts of ether byproducts (Table 5, Entries 1–6 and 8–13). As for substrates **3d** and **3g** having electron-donating substituents at the *para* position of the benzene rings, the corresponding products were attained in moderate yields (Table 5, Entries 4 and 8). Using MCP monoaryl alcohols **3h** and **3i** as well as MCP monoalkyl alcohols **3j** and **3k** as the substrates, the reaction also proceeded smoothly to give the corresponding products **4h** and **4i** as well as **4j** and **4k** in good yields with *anti* configuration under the standard conditions, presumably due to steric effects (Table 5, Entries 9–12).[8] Only in the case of *Z*-MCP dimethyl alcohol **3a** was a complex mixture formed, presumably also due to steric effects in the alkyl migration (Table 5, Entry 7).

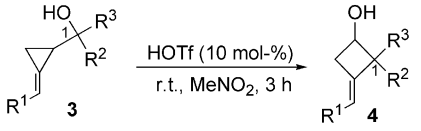
Table 4. Optimization of the reaction conditions of MCP dimethyl alcohol **3a**.



Entry	Catalyst	Solvent	4a/4a'	Yield [%][a] 4a+4a'
1	HOTf	DCE	1.6:1	85
2	$BF_3{\cdot}Et_2O$	DCE	1.5:1	85
3	CF_3COOH	DCE	1.5:1	53
4	HOTf	hexane	1:1.8	88
5	HOTf	DCE	1.4:1	86[b]
6	HOTf	$MeNO_2$	6.0:1	85

[a] Isolated yield. [b] 2.0 equiv. of H_2O was added.

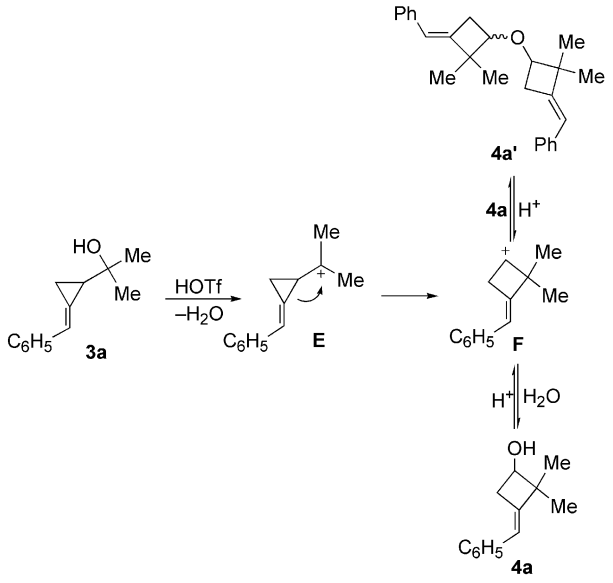
Table 5. Ring-opening reaction of various MCP alkyl alcohols.



Entry	$R^1/R^2/R^3$	Yield [%][a] 4
1	**3a**, C_6H_5/Me/Me	**4a**, 72
2	**3b**, *p*-BrC_6H_4/Me/Me	**4b**, 62
3	**3c**, *p*-ClC_6H_4/Me/Me	**4c**, 65
4	**3d**, *p*-MeC_6H_4/Me/Me	**4d**, 38
5	**3e**, *p*-$C_6H_5C_6H_4$/Me/Me	**4e**, 68
6	**3f**, *m*-MeC_6H_4/Me/Me	**4f**, 52
7	Z-**3a**/C_6H_5/Me/Me	complex mixture
8	**3g**, 3,4,5-$(MeO)_3C_6H_2$/Me/Me	**4g**, 40
9	**3h**, C_6H_5/C_6H_5/H	**4h**, 58[b]
10	**3i**, C_6H_5/*p*-MeC_6H_4/H	**4i**, 56[b]
11	**3j**, C_6H_5/Me/H	**4j**, 63[b]
12	**3k**, C_6H_5/Et/H	**4k**, 70[b]
13	**3l**, C_6H_5/Et/Et	**4l**, 70

[a] Isolated yield. [b] The product was obtained exclusively with the *anti* configuration.

A plausible reaction mechanism for this intramolecular ring enlargement is shown in Scheme 5 by using **3a** as a model. In situ generated cationic intermediate **E** undergoes ring enlargement to give intermediate **F**, which produces **4a** through reaction with water. The reaction of intermediate **F** with **4a** affords byproduct **4a′**. It should be noted that both the transformations of **F** into **4a** and **F** into **4a′** are reversible in the presence of H^+, and when a strong polar solvent ($MeNO_2$) is used, H^+ can react with **F** more easily than **4a**, giving **4a** as the major product.



Scheme 5. A plausible reaction mechanism.

Comparing the formation of **2** and **4** in Schemes 4 and 5, we thought that steric effects played an important role in the manner in which bond cleavage occurred in the MCP alcohols. MCP diaryl alcohols preferred to undergo a ring-opening process to release ring strain, whereas the MCP monoaryl alcohols and dialkyl alcohols tended to undergo cation-induced ring enlargement.

Conclusions

We have found a novel ring-opening/ring-expansion rearrangement of MCP diaryl alcohols **1** or dialkyl- and monoalkyl- as well as monoaryl alcohols **3** catalyzed by the Brønsted acid HOTf under mild conditions, affording interesting multisubstituted naphthalene derivatives **2** and cyclobutanol derivatives **4** in moderate to good yields. In addition, in the reactions of MCP monoaryl alcohols **3h** and **3i**, none of the naphthalene products was observed. The plausible reaction mechanisms have been discussed and the wide substrate scope has been indicated. The potential utilization of the products and the extension of the scope of the methodology are currently under investigation.

Experimental Section

General Procedure for the Rearrangement of MCP Aryl and Alkyl Alcohols: A Schlenk tube was charged with MCP aryl alcohol **1a** (0.2 mmol, 62.4 mg) in DCE (2.0 mL) or MCP alkyl alcohol **3a** (0.2 mmol, 39.6 mg) in CH_3NO_2 (2.0 mL). The mixture was cooled to 0 °C (room temp. for CH_3NO_2), and then HOTf (3.0 mg, 10 mol-%) was added by syringe. The reaction was stirred at 0 °C for 3 h. The solvent was removed under reduced pressure, and then the residue was purified by a flash column chromatography.

Compound 2a: Yield: 34 mg, 88%. This is a known compound.[7] ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.26 (s, 3 H, CH_3), 7.31–7.35 (m, 4 H, Ar), 7.38 (s, 1 H, Ar), 7.41–7.57 (m, 9 H, Ar), 7.89–7.92 (m, 1 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 20.8, 124.8, 125.6, 125.8, 126.5, 127.0, 127.2, 128.2, 128.4, 129.7, 130.0, 130.1, 130.2, 132.6, 133.2, 137.8, 139.4, 139.8, 140.8 ppm.

Compound 4a: Yield: 22 mg, 63%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.23 (s, 6 H, $2CH_3$), 1.78 (d, J = 6.8 Hz, 1 H, OH), 2.91–2.97 (m, 1 H), 3.31–3.37 (m, 1 H), 4.05–4.10 (m, 1 H), 6.19–6.20 (m, 1 H, CH), 7.17 (dd, J = 7.2, 7.2 Hz, 1 H, Ar), 7.21 (d, J = 7.2 Hz, 2 H, Ar), 7.31 (dd, J = 7.2, 7.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 20.9, 25.1, 39.8, 50.3, 72.8, 119.7, 126.2, 127.3, 128.4, 137.6, 146.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3562, 3391, 3084, 3057, 3024, 2956, 2923, 2862, 1679, 1598, 1490, 1460 cm^{-1}. MS (EI): *m*/*z* (%) = 188 (9.8) $[M]^+$, 155 (16.9), 129 (30.1), 117 (21.8), 86 (48.4), 84 (76.0), 51 (35.7), 49 (100.0). HRMS (EI): calcd. for $C_{13}H_{16}O$ $[M]^+$ 188.1201; found 188.1202.

Compound 4a′: Yield: 5 mg, 13%. Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ = 1.26 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 2.99–3.06 (m, 1 H), 3.21–3.27 (m, 1 H), 3.75 (t, J = 7.2 Hz, 1 H), 6.18 (br. s, 1 H, CH), 7.16 (dd, J = 7.2, 7.2 Hz, 1 H, Ar), 7.22 (d, J = 7.2 Hz, 2 H, Ar), 7.30 (dd, J = 7.2, 7.2 Hz, 2 H, Ar) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ = 21.4, 21.7, 25.8, 26.0, 37.6, 37.7, 50.2, 50.3, 77.2, 77.9, 119.2, 119.3, 126.1, 127.3, 128.4, 137.7, 137.8, 146.2, 146.7 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3056, 3024,

2957, 2926, 2861, 1599, 1492, 1459, 1428, 1380, 1104 cm^{-1}. MS (EI): *m*/*z* (%) = 187 (33.6) $[M - 171]^+$, 171 (48.7), 143 (54.4), 129 (100.0), 128 (32.7), 117 (18.3), 115 (27.5), 91 (28.3). HRMS (EI): calcd. for $C_{13}H_{16}O$ $[M - 170]^+$ 188.1201; found 188.1200.

Supporting Information (see footnote on the first page of this article): General remarks, reaction procedures, and spectroscopic data of all prepared compounds.

Acknowledgments

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