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# Solvent-free, $AlCl_3$-promoted tandem Friedel–Crafts reaction of arenes and aldehydes

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**Abstract**

Tandem Friedel–Crafts reaction of arenes and aldehydes under the catalysis of Lewis acid was investigated. Both aromatic and aliphatic aldehydes underwent a tandem Friedel–Crafts alkylation with electron-rich arenes to afford 1,1,1-triaryl/1,1-diarylalkanes in the presence of anhydrous aluminum chloride under solvent-free conditions. The scope, limitation, and mechanism of the tandem reaction were also discussed.


*Keywords:* Alcohol; Aldehyde; Aluminum chloride; Arene; Friedel–Crafts alkylation; Solvent-free; Tandem reaction

## 1. Introduction

Friedel–Crafts alkylation is one of important and convenient reactions used in the preparation of alkyl substituted arenes [1]. Generally, alkyl halide, alkyl sulfonate, alkene, alcohol, and alkene oxide were used as alkylation reagents in the Friedel–Crafts alkylation [1]. However, several examples of the Friedel–Crafts alkylation of arenes with ketones [2] and *N*-arylsulfonyl aldimines [3] as alkylation reagents were observed. In a few cases, aromatic aldehydes were also found to be used in the Friedel–Crafts alkylation, especially for electron-rich arenes and aromatic heterocyclic compounds, such as phenols [4], indoles [5], pyrroles [6], and furans and thiophenes [7], etc. It has been well-known that formaldehyde could undergo a Friedel–Crafts reaction with benzene to yield benzyl chloride in the presence of anhydrous zinc chloride and hydrogen chloride via benzyl alcohol as an intermediate, called chloromethylation reaction. It is also known that the reaction of benzaldehyde and benzene produced diphenylmethanol, which could further yield triphenylmethane under the catalysis of anhydrous aluminum chloride [8]. Recently we investigated tandem Friedel–Crafts acylation and alkylation of arenes with acyl chlorides and α,β-unsaturated acyl chlorides, respectively, in the presence of anhydrous aluminum chloride [9]. Strong proton acid-catalyzed tandem Friedel–Crafts reactions of arenes and aromatic aldehydes have been reported [10]. $LnCl_3$ (Ln = Pr, Dy, Er, Sm, Yb) and $Yb(O_3SCF_3)_3$ catalyzed the electrophilic alkylation of PhR (R = H, Me) with AcCl–PhCHO has also been reported [11]. The paper indicated that the reaction proceeded stepwise to give $PhCH(CH_6H_4R)_2$ and $LnCl_3$ did not catalyze ordinary Friedel–Crafts acylation. To further investigate Friedel–Crafts alkylation of arenes with aldehydes under the catalysis of Lewis acids (LAs), we systematically studied the reaction and wish to report the results on this reaction and discuss its scope, limitation, and mechanism.

## 2. Experimental

### 2.1. General methods

Melting points were measured on a Yanaco MP-500 melting point apparatus and are uncorrected. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on a Varian Mercury Plus 300 (300 MHz) spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were obtained on a VG-ZAB-HS mass spectrometer. IR spectra were recorded on a Nicolet AVATAR 330 FT–IR spectrometer with an OMNI sampler. CHN analyses were carried out on an Elementar Vario EL analyzer.

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### 2.2. General procedure for $AlCl_3$-promoted tandem Friedel–Crafts alkylation of arenes and aldehydes

To a mixture of anhydrous aluminum chloride (0.16 g, 1.2 mmol)(0.20 g, 1.5 mmol for aliphatic aldehyde) and arene (6 mmol for aromatic aldehyde, 3 mmol for aliphatic aldehyde) was added aldehyde (3 mmol) dropwise at RT. The resulting mixture was kept stirring for 4 h (for aromatic aldehyde) or 12 h (for aliphatic aldehyde). It was carefully decomposed with water (10 mL) and extracted with ether (10 mL × 3). After dried over $Na_2SO_4$, upon evaporation of the dried ether the residue was purified on silica gel column with a mixture of petroleum ether (60–90 °C) and ethyl acetate (40:1, v/v) as eluent to afford the desired product.

### 2.3. (4-Methylthiophenyl)-phenylmethanol (**3a**)

Colorless crystals, m.p. 93.5–95 °C ([12], m.p. 99 °C). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.45 (s, 3H, $CH_3$), 5.78 (s, 1H, CH), 7.20–7.42 (m, 9H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 15.8, 75.8, 126.4, 126.6, 127.0, 127.6, 128.5, 137.6, 140.7, 143.6.

### 2.4. 2-Methyl-1-(4-methylthiophenyl)-propan-1-ol (**3h**)

Colorless oil. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.79 (d, $J$ = 7.2 Hz, 3H, $CH_3$), 0.97 (d, $J$ = 6.8 Hz, 3H, $CH_3$), 1.76 (br s, 1H, OH), 1.91 (m, 1H, CH), 2.48 (s, 3H, $SCH_3$), 4.32 (dd, $J$ = 3.0, 7.0 Hz, 1H, OCH), 7.23 (s, 4H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 15.9, 18.2, 18.9, 35.2, 79.6, 126.4, 127.1, 137.2, 140.5. MS (EI) *m/z*: 196 ($M^+$, 10), 153 (75), 109 (20), 86 (63), 84 (100), 47 (31); IR $\upsilon$ ($cm^{-1}$): 3438 (OH), 2964, 2873, 1469, 758. Anal. Calcd for $C_{11}H_{16}OS$: 196.0922. Found: 196.0917.

### 2.5. 2-Methyl-1-(4-methylthiophenyl)-propan-2-ol (**3h′**)

Colorless crystals; m.p. 56–57 °C. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.22 (s, 6H, $2CH_3$), 2.48 (s, 3H, $SCH_3$), 2.73 (s, 2H, $CH_2$), 7.12–7.26 (m, 4H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 16.0, 29.1, 49.1, 70.7, 126.6, 130.9, 134.7, 136.2. MS (EI) *m/z*: 196 ($M^+$, 22), 181 (12), 138 (100), 123 (87), 91 (36), 59 (88); IR $\upsilon$ ($cm^{-1}$): 3425 (OH), 2969, 1493, 1128. Anal. Calcd for $C_{11}H_{16}OS$: C, 67.30; H, 8.22. Found: C, 67.00; H, 8.06.

### 2.6. (4-Fluorophenyl)-bis (4-methylthiophenyl)methane (**4b**)

Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.44 (s, 6H, $2CH_3$), 5.42 (s, 1H, CH), 6.95-7.10 (m, 8H, ArH), 7.17 (d, $J$ = 6.8 Hz, 4H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 15.8, 54.9, 115.1 (d, $J$ = 21.3 Hz), 126.7, 129.7, 130.7 (d, $J$ = 7.6 Hz), 136.5, 139.3 (d, $J$ = 3.5 Hz), 140.5, 161.4 (d, $J$ = 244 Hz). MS (EI) *m/z*: 354 ($M^+$, 100), 307 (73), 259 (40), 231 (30), 183 (49), 165 (14). Anal. Calcd for $C_{21}H_{19}FS_2$: 354.0912. Found: 354.0913.

### 2.7. (4-Chlorophenyl)-bis (4-methylthiophenyl)methane (**4c**)

Colorless oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.46 (s, 6H, $2CH_3$), 5.42 (s, 1H, CH), 7.00 (d, $J$ = 8.1 Hz, 4H, ArH), 7.03 (d, $J$ = 6.9 Hz, 2H, ArH), 7.18 (d, $J$ = 8.1 Hz, 4H, ArH), 7.26 (d, $J$ = 6.9 Hz, 2H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 15.8, 55.0, 126.6, 128.5, 129.7, 130.6, 136.5, 140.1, 142.1. MS (EI) *m/z*: 370 ($M^+$, 100), 323 (68), 259 (31), 247 (29), 199 (24), 165 (47), 124 (31). Anal. Calcd for $C_{21}H_{19}ClS_2$: 370.0617. Found: 370.0611.

### 2.8. Bis(4-methylthiophenyl)(4-nitrophenyl)methane (**4d**)

Yellowish crystals; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.47 (s, 6H, $2CH_3$), 5.55 (s, 1H, CH), 7.00 (d, $J$ = 8.4 Hz, 4H, ArH), 7.20 (d, $J$ = 8.4 Hz, 4H, ArH), 7.27 (d, $J$ = 8.4 Hz, 2H, ArH), 8.14 (d, $J$ = 8.4 Hz, 2H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 15.7, 55.5, 123.6, 126.6, 129.6, 130.1, 137.2, 138.9, 146.5, 151.3. MS (EI) *m/z*: 381 ($M^+$, 100), 334 (50), 259 (37), 165 (26), 152(12). Anal. Calcd for $C_{21}H_{19}NO_2S_2$: C, 66.11; H, 5.02, N, 3.67. Found: C, 66.12; H, 5.01; N, 3.68.

### 2.9. Bis(4-methylthiophenyl)(2-nitrophenyl)methane (**4f**)

Yellowish oil; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.46 (s, 6H, $2CH_3$), 6.20 (s, 1H, CH), 6.97 (d, $J$ = 6.6 Hz, 4H, ArH), 7.10 (d, $J$ = 9.3 Hz, 1H, ArH), 7.18 (d, $J$ = 8.4 Hz, 4H, ArH), 7.36–7.90 (m, 3H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 15.6, 50.3, 124.8, 126.5, 127.6, 129.8, 131.8, 132.5, 137.0, 137.9, 138.6, 149.6. MS (EI) *m/z*: 381 ($M^+$, 100), 364 (68), 347 (47), 317 (67), 287 (30), 239 (34), 195 (27), 151 (58). Anal. Calcd for $C_{21}H_{19}NO_2S_2$: 381.0857. Found: 381.0860.

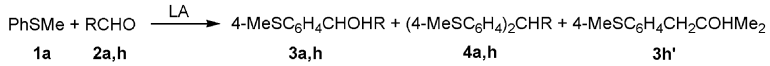
### 2.10. Bis(4-methylthiophenyl)(naphth-2-yl)methane (**4g**)

Colorless crystals; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 2.44 (s, 6H, $2CH_3$), 6.17 (s, 1H, CH), 6.94 (d, $J$ = 6.7 Hz, 1H, ArH), 7.02 (d, $J$ = 8.4 Hz, 4H, ArH), 7.15 (d, $J$ = 8.4 Hz, 4H, ArH), 7.18–7.44 (m, 3H, ArH), 7.75 (d, $J$ = 8.1 Hz, 1H, ArH), 7.85 (d, $J$ = 8.4 Hz, 1H, ArH), 7.94 (d, $J$ = 7.8 Hz, 1H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 15.7, 52.0, 124.2, 125.2, 125.5, 126.1, 126.5, 127.38, 127.43, 128.7, 130.0, 131.7, 133.9, 136.2, 139.5, 140.5. MS (EI) *m/z*: 386 ($M^+$, 100), 339 (34), 292 (11), 259 (18), 216 (21), 215 (57). Anal. Calcd for $C_{25}H_{22}S_2$: C, 77.67; H, 5.74. Found: C, 77.71; H, 5.66.

### 2.11. 2-Methyl-1,1-bis(4-methylthiophenyl)propane (**4h**)

Colorless crystals; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 0.99 (s, 9H, $3CH_3$), 2.42 (s, 6H, $2CH_3$), 3.62 (s, 1H, CH), 7.16 (d, $J$ = 8.4 Hz, 4H, ArH), 7.32 (d, $J$ = 8.4 Hz, 4H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 16.0, 21.7, 31.7, 60.0, 126.9, 128.4, 135.4, 141.9. MS (EI) *m/z*: 302 ($M^+$, 16), 259 (100), 244 (9), 197 (10), 165 (23), 152 (5), 129 (5), 43 (5). Anal. Calcd for $C_{18}H_{22}S_2$: C, 71.47; H, 7.33. Found: C, 71.28; H, 7.46.

Table 1
Friedel–Crafts reaction of thioanisole and benzaldehyde in the presence of Lewis acid[a]




| Entry | R | LA | **1**:**2**:LA | *T* (°C) | Time (h) | **3** Yield[b] (%) | **3′** Yield[b] (%) | **4** Yield[b] (%) |
|---|---|---|---|---|---|---|---|---|
| 1[c] | Ph | $AlCl_3$ | 2:1:3 | RT | 22 | 16 | | 24 |
| 2 | Ph | $AlCl_3$ | 1:1:1 | RT | 4 | 12 | | 57 |
| 3 | Ph | $AlCl_3$ | 2:1:1 | RT | 4 | | | 70 |
| 4 | Ph | $AlCl_3$ | 2:1:0.4 | RT | 4 | | | 69 |
| 5 | Ph | $AlCl_3$ | 2:1:3 | 0 | 22 | <5% | | <5% |
| 6 | Ph | $FeCl_3$ | 1:1:2 | RT | 48 | <10% | | <10% |
| 7 | Ph | $FeCl_3$ | 2:1:0.4 | RT | 4 | | | 27 |
| 8 | Ph | $ZnCl_2$ | 1:1:2 | RT | 48 | – | | – |
| 9[c] | *i*-Pr | $AlCl_3$ | 1:1:1 | RT | | 6 | 5 | 47 |
| 10 | *i*-Pr | $AlCl_3$ | 1:1:1 | RT | | | | 30 |
| 11 | *i*-Pr | $AlCl_3$ | 2:1:1.5 | RT | | | | 19 |
| 12 | *i*-Pr | $AlCl_3$ | 2:1:0.5 | RT | | | | 23 |
| 13 | *i*-Pr | $AlCl_3$ | 1:1:0.5 | RT | | | | 51 |

[a] Reaction conducted in 3 mmol scale of aldehyde.
[b] Isolated yield after column chromatography.
[c] Conducted in $CS_2$.

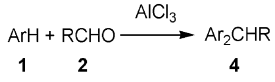
### *2.12. 2,2-Dimethyl-1,1-bis (4-methylthiophenyl)propane (**4i**)*

Colorless crystals; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 1.00 (s, 9H, $3CH_3$), 2.44 (s, 6H, $2CH_3$), 3.63 (s, 1H, CH), 7.17 (d, $J$ = 8.2 Hz, 4H, ArH), 7.33 (d, $J$ = 8.2 Hz, 4H, ArH). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$: 16.0, 29.1, 35.1, 63.2, 126.4, 130.2, 135.6, 140.0. MS (EI) *m*/*z*: 316 ($M^+$, 8), 259 (100), 244 (8), 197 (10), 165 (24), 57 (16), 41 (19). Anal. Calcd for $C_{19}H_{24}S_2$: C, 72.10; H, 7.64. Found: C, 72.10; H, 7.61.

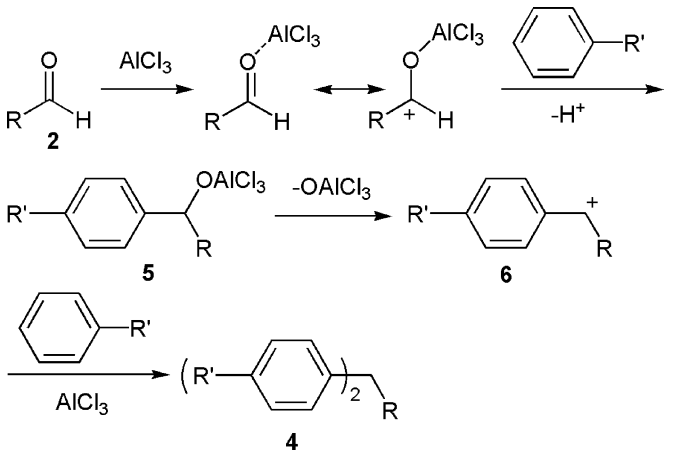
## 3. Results and discussion

As part of an ongoing program to investigate onto the Friedel–Crafts alkylation of arenes with ketones and aldehydes, we firstly conducted the Friedel–Crafts acylation of a more electron-rich arene, thioanisole, with benzaldehyde as a model reaction to optimize the reaction conditions and hoped to be able to control the reaction conditions to afford diarylmetanol and triarylmethane, respectively. The results are summarized in Table 1. It was observed that, although 4-methylthiophenylphenylmethanol (**3a**) could be obtained in some cases, its yield always is low (Table 1, entries 1, 2, 5, and 6). In most cases, bis(4-methylthiophenyl)phenylmethane (**4a**) was obtained as major product, even sole product (Table 1, entries 3, 4, and 7). Satisfactory yield of triarylmethane was achieved at room temperature (RT). No improvement was observed at higher temperature (detailed results not shown). For aliphatic aldehyde, isobutanal, except for normal thioanisole-alkylated product 2-methyl-1,1-bis(4-methylthiophenyl)propan-1-ol (**3h**), a rearrangement alcohol, 2-methyl-1,1-bis(4-methylthiophenyl)propan-2-ol (**3h′**), was also obtained when the reaction was conducted in the solvent

Table 2
Solvent-free, $AlCl_3$-promoted tandem Friedel–Crafts alkylation of arenes and aldehydes




| Entry | **1**:**2**:$AlCl_3$ | Product | Ar | R | m.p. (°C) | Yield (%) |
|---|---|---|---|---|---|---|
| 1 | 2:1:1 | **4a** | 4-$MeSC_6H_4$ | Ph | 70–70.5 ([16], 63.4) | 70 |
| 2 | 2:1:0.4 | **4b** | 4-$MeSC_6H_4$ | 4-$FC_6H_4$ | Oil | 77 |
| 3 | 2:1:0.4 | **4c** | 4-$MeSC_6H_4$ | 4-$ClC_6H_4$ | Oil | 75 |
| 4 | 2:1:0.4 | **4d** | 4-$MeSC_6H_4$ | 4-$O_2NC_6H_4$ | 100–101 | 71 |
| 5 | 2:1:0.4 | **4e** | 4-$MeSC_6H_4$ | 4-$MeOC_6H_4$ | 54.5–55.5 ([17], 79-82) | 26 |
| 6 | 2:1:0.4 | **4f** | 4-$MeSC_6H_4$ | 2-$O_2NC_6H_4$ | Oil | 24 |
| 7 | 2:1:0.4 | **4g** | 4-$MeSC_6H_4$ | 2-Naphthyl | 117–119 | 6 |
| 8 | 1:1:0.5 | **4h** | 4-$MeSC_6H_4$ | $Me_2CH$ | 93–96 | 51 |
| 9 | 1:1:0.5 | **4i** | 4-$MeSC_6H_4$ | $Me_3C$ | 72–73 | 55 |
| 10 | 2:1:0.4 | **4j** | 4-$Me_2NC_6H_4$ | Ph | 105.5–107 ([18], 99) | 51 |
| 11 | 2:1:0.4 | **4k** | 4-$MeOC_6H_4$ | Ph | 104.5–105.5 ([19], 100.5–101.5) | 49 |
| 12 | 2:1:0.4 | | 4-$MeC_6H_4$ | Ph | | – |
| 13 | 2:1:0.4 | | Ph | Ph | | – |
| 14 | 2:1:0.4 | | 4-$MeC_6H_4$ | 4-$ClC_6H_4$ | | – |
| 15 | 2:1:0.4 | | Ph | 4-$O_2NC_6H_4$ | | – |




Scheme 1. Suggested mechanism for the $AlCl_3$-promoted tandem Friedel–Crafts alkylation of arenes and aldehydes.

carbon disulfide (Table 1, entry 9). However, no any alcohol was observed under solvent-free conditions (Table 1, entries 10–13). Anhydrous aluminum chloride has been found to be the most efficient catalyst for this reaction.

The current reaction provides a convenient and practical route to preparing triaryl methanes in good yield from arenes and aromatic aldehydes in the presence of anhydrous aluminum chloride. Triaryl methanes display various and interesting properties and have received a great deal of attention as leuco dyes [13], photochromic agents [14], suitable building blocks for generating dendrimers [15], etc. This promotes us to investigate the generality of this reaction. A series of $AlCl_3$-promoted tandem Friedel–Crafts alkylation of arenes and aldehydes were attempted. The results are presented in Table 2. The results indicate that the electron-rich arenes gave rise to triaryl methanes in satisfactory to good yields with aromatic aldehydes, especially with the electron-deficient aromatic aldehydes (Table 2, entries 1–7, 10, and 11). They produced 1,1-diarylalkanes in good yields with aliphatic aldehydes (Table 2, entries 8 and 9). Even for 2,2-dimethylpropanal, no rearrangement product was observed under current solvent-free conditions (Table 2, entry 9). However, for arenes with weak electron-donating or electron-withdrawing groups, such as, toluene, benzene, halobenzenes, no reaction occurred, even with electron-deficient aromatic aldehydes, such as 4-chlorobenzaldehyde and 4-nitrobenzaldehyde (Table 2, entries 12–15).

Considering on the reaction mechanism, it was assumed that, firstly, the carbonyl group of aldehydes coordinates with aluminum chloride, and then undergoes a Friedel–Crafts alkylation with arenes to yield aluminum 1-aryl-1-alkoxide **5**, which could eliminate $^{-}OAlCl_3$ to form benzylic carbocations. The formed carbocations further undergo a Friedel–Crafts alkylation with arenes to generate 1,1-diaryl/1,1,1-triarylalkanes (Scheme 1). On the other hand, the reaction of isobutanal with anisole in carbon disulfide under the catalysis of aluminum chloride to produce 1,1-bis(4-methylthiophenyl)-2-methylpropane (**4h**, 47%), 1-(4-methylthiophenyl)-2-methylpropan-1-ol (**3h**, 6%), and 1-(4-methylthiophenyl)-2-methylpropan-2-ol (**3h′**, 5%) (Table 1, entry 9). These results support our proposed mechanism and indicate that the in situ formed benzylic carbocations are more active alkylating reagents than aldehydes in the Friedel–Crafts alkylation. The current results also indicate that the alkylation of the benzylic carbocations is faster than the rearrangement of carbocations, especially under solvent-free conditions.

In the reaction, the electron-donating groups, such as methylthio group MeS, could stabilize the formed carbocation intermediates **6** via the formation of octet structural intermediates due to the existence of sulfur donating conjugative effect. Thus, the electron-rich arenes are more active than the electron-deficient arenes. Our results also indicate that alkylthiobenzenes are more active than alkoxybenzenes in the tandem reaction because alkylthio groups are more electron-donating groups than alkoxy groups.

## 4. Conclusions

In summary, tandem Friedel–Crafts alkylation of arenes and aldehydes in the presence of Lewis acids was investigated. Both aromatic and aliphatic aldehydes underwent a tandem Friedel–Crafts alkylation with electron-rich arenes to afford 1,1,1-triaryl/1,1-diarylalkanes in the presence of anhydrous aluminum chloride under solvent-free conditions. The scope, limitation, and mechanism of the reaction were discussed on the basis of the designed experiments. The current reaction provides a convenient, environment-friendly, and practical route to the preparation of 1,1-diaryl/1,1,1-triarylalkanes from arenes and aldehydes.

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