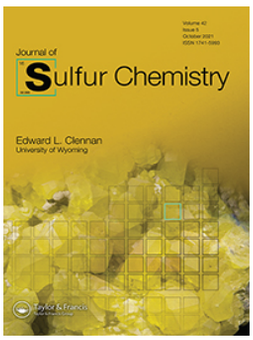

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# Direct synthesis of sulfinic esters via ultrasound accelerated tandem reaction of thiols and alcohols with *N*-bromosuccinimide

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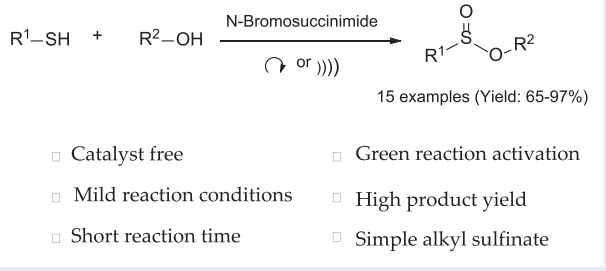
**ABSTRACT**

The direct transformation of various thiols and simple alcohols with N-bromosuccinimide into sulfinic esters has been investigated by using different categories of base/acidic catalysts as well as co-solvents under varied reaction conditions. The reaction was found out to afford the sulfinic esters with high yields in the absence of catalysts, especially within the shorter time under the acceleration of ultrasonic irradiation than under the longer-lasting conventional stirring conditions.

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**KEYWORDS**
Thiols; sulfinic esters; *N*-bromosuccinimide; tandem reaction; ultrasound irradiation

## 1. Introduction

Sulfinic esters (general formula: $R^1$-S(O)-O-$R^2$), the esters of sulfinic acids, are intermediates in the organosulfur chemistry, especially in the synthesis of sulfoxides [1,2], sulfonamides [3,4], sulfonimidates [4], and sulfonyl isonitriles (TosMIC analogs) [5]. Moreover, sulfinate salts are also used as efficient reagents in the electrochemical sulfonylation of alkynes [6]; or in the radically alkylated electrophilic olefins with iridium(III)-complex as a photocatalyst [7].

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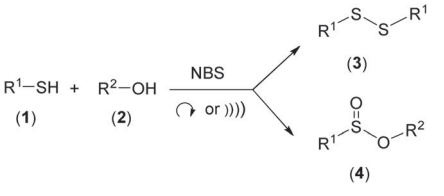
Various indirect synthetic pathways of sulfinic acid esters from the sulfur(IV) derivatives have been performed via the nucleophilic substitution of alcohols/alkoxytrimethylsilane into sulfinyl chloride [8–13], sulfinamide [14–16], and sulfinyl sulfone [17]. Furthermore, the reaction of sulfinic acid with alcohols [18–20], the Brønsted/Lewis acid-catalyzed sulfination of alcohols by using sulfinic acid sodium salts [21–22], or by using *p*-toluenesulfonylmethyl isocyanide [23–25], the copper-catalyzed aerobic oxidative reaction [26,27], the esterification of sulfonyl hydrazides with alcohols promoted by $NaHSO_3$ [28], the decomposition of N–sulfonylhydrazones mediated by Wittig ylide [29], or DIPEA (di-*iso*-propylethylamine) [30], as well as the *in situ* reduction of sulfonyl chlorides with alcohols in the presence of excess trimethyl phosphite have been also developed for the synthesis of sulfinic esters [31]. Recently, the alcoholysis of sulfinyl bromide *in situ* formed from the C-S(O) bond cleavage of sulfone-bearing *t*-butyl group by using N-bromosuccinimide was found out by Wei and co-workers [32]. Other popular pathways for the syntheses of sulfinic esters from the sulfur (II) derivatives, *e.g.* disulfides have attracted attention via the chlorination of disulfides in alcohols [33], and the oxidation of disulfides in alcohols by using N-bromosuccinimide [34], and lead tetraacetate [35]. Unfortunately, the sulfur (IV) derivatives are commercially available within limit, except for sulfinate salts. In addition, the sulfur (II) derivatives as disulfides are popularly prepared via the oxidative coupling of thiols by utilizing various oxidizing agents, *e.g.* N-bromosuccinimide [36].

In recent years, the direct transformations of thiols and alcohols to sulfinic esters have become interesting topics, for instance they were performed with oxygen in the presence of several catalysts, *e.g.* copper(I) iodide and 1,5,7-triazabicyclo[4.4.0]dec-5-ene [37], cobalt nanocatalyst supported on N-$SiO_2$-doped activated carbon [38], or performed with N-bromosuccinimide at 0–25°C for several hours [5,39–40]. Furthermore, other processes such as electrochemistry [41–44], and photochemistry [45] have also been introduced for the direct synthesis of sulfinates.

Therefore, our intentions with this work were to improve and understand the synthetic pathway of sulfinic esters via an ultrasonic-assisted tandem reaction of thiols and alcohols with N-bromosuccinimide to achieve maximum yield of the desired product with respect also to the short reaction time at room temperature (Scheme 1). Although sulfinic esters synthesized from the reactions of thiols and alcohol with NBS have been announced [2,5,39–40], the impact factors such as the molar ratio of thiols, alcohols and NBS, the amount of solvent, the type of co-solvent or catalyst, and the nature of thiols as well




$R^1$ = $C_6H_5$, $C_6H_5CH_2$, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$ClC_6H_4$, *n*-$C_4H_9$, *n*-$C_8H_{17}$, c-$C_6H_{11}$

$R^2$ = $CH_3$, $C_2H_5$, *n*-$C_3H_7$, *i*-$C_3H_7$, *n*-$C_4H_9$.

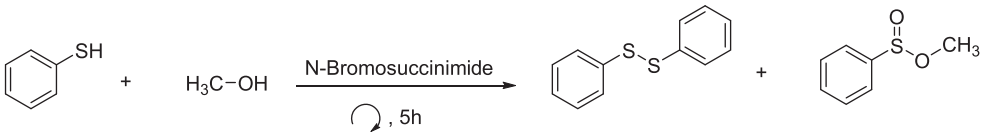
**Scheme 1.** The transformation of thiols and alcohols into sulfinic esters in the presence of *N*-Bromosuccinimide.

as alcohols have not been considered extensively to assimilate, illustrate the scope and generality of this process.

## 2. Result and discussion

At the beginning of our work, the priority adding of reactants was investigated and selected by sequentially dropping thiol (3 mmol) in methanol (5 mL), NBS (4.5 mmol) in methanol (9 mL) and a specific volume of co-solvents *e.g.* dichloromethane, ethyl acetate, [Bmim]Br or [Bmim]$BF_4$ into the reaction flask at room temperature. The amount of NBS was deliberately used in the lower amount (6.0 mmol) than those in the previous literature [2,5], so that the effects of catalyst or co-solvent on the reaction of thiophenol and methanol with NBS were found out clearly. The results depicted in Entries 1–5, Table 1 showed that the presence of [Bmim]$BF_4$ led to a weight loss of product, and dichloromethane as well as [Bmim]Br reduced the formation of sulfinate slightly in comparison with the case of using only methanol. Among above co-solvents, ethyl acetate was selected as the best co-solvent for this reaction. In the further experiments, inorganic solid supports such as silica gel, alumina and Mont K-10 were alternatively tested for the reaction optimization. The results showed that diphenyl disulfide was mainly formed instead of sulfinate in the presence of above inorganic solid supports, exceptionally Mont K10. In the next survey, acidic/base catalysts such as triethylamine, Amberlyst 26 and Amberlyst 15 used have not increased efficiency in the product formation. Consequently, neither catalysts nor inorganic solid supports were selected for the reaction of thiophenol and methanol with N-bromosuccinimide (Entries 6–13, Table 1).

**Table 1.** Influence of reaction condition on the yield of methyl benzenesulfinate obtained by the tandem reaction of thiophenol and methanol with *N*-Bromosuccinimide.




**1a** **2a** **3a** **4a**

| Entry | Reaction condition | Conv. (%) | Yield (%)[b] 4a | 3a |
|---|---|---|---|---|
| 1 | NBS | 98 | 52 | 26 |
| 2 | NBS in $CH_2Cl_2$ (1 mL)s | 96 | 46 | 24 |
| 3 | NBS in EtOAc (1 mL) | 100 | 64 | 14 |
| 4 | NBS in [Bmim]Br (3 mmol) | 100 | 52 | 33 |
| 5 | NBS in [Bmim]$BF_4$ (3 mmol) | 100 | 26 | 13 |
| 6 | NBS/$SiO_2$ (wt. 25%) (3.203 g) | 100 | 23 | 52 |
| 7 | NBS/$SiO_2$ (wt. 50%) (1.602 g) | 100 | 2 | 73 |
| 8 | NBS/$SiO_2$ (wt. 75%) (1.068 g) | 100 | 0 | 85 |
| 9 | NBS/$Al_2O_3$ (wt. 25%) (3.203 g) | 100 | 6 | 46 |
| 10 | NBS/Mont K-10 (wt. 25%) (3.203 g) | 100 | 64 | 30 |
| 11 | NBS catalyzed by $Et_3N$ (1.5 mmol) | 100 | 60 | 27 |
| 12 | NBS catalyzed by Amberlyst 26 (1.5 mmol) | 100 | 58 | 26 |
| 13 | NBS catalyzed by Amberlyst 15 (1.5 mmol) | 100 | 60 | 24 |

Note: The reaction of thiophenol (3 mmol), MeOH (5 mL), NBS (4.5 mmol) dissolved in an additional MeOH (9 mL) and a specific co-solvent/catalyst was performed under magnetic stirring at room temperature for 5 h.

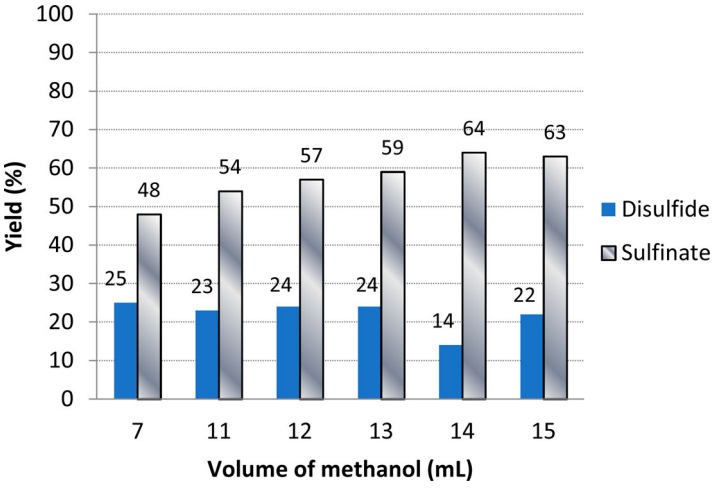


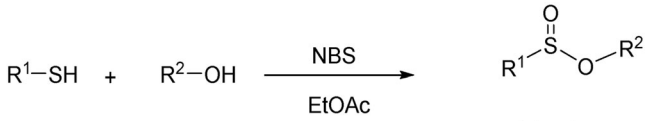

**Figure 1.** Influence of the methanol amount on the tandem reaction of thiophenol and methanol with *N*-bromosuccinimide to obtain methyl benzenesulfinate under magnetic stirring at room temperature (5 h, thiophenol: 3.0 mmol, NBS: 4.5 mmol, EtOAc: 1 mL).

In the next series of experiments, the volume of methanol was studied in order to get the higher yield of methyl benzenesulfinate. The results, depicted in Figure 1, also demonstrated that the amount of methanol influenced slightly on the yield of methyl sulfinate and finally was selected at 14 mL for the next investigation (Figure 1).

Subsequently, the influences of the molar ratios between thiophenol and *N*-bromosuccinimide were investigated. The results displayed that when the amount of *N*-bromosuccinimide varied from 4.5 mmol to 6.0 mmol, the yield of methyl benzenesulfinate was achieved from 64% (Entry 3, Table 1) to 87% after 5 h-stirring at room temperature in MeOH (14 mL) and EtOAc (1 mL). In the next experiments, the factor of reaction time was studied in four activation methods: stirring method, ultrasound irradiation, conventional heating and microwave irradiation. Consequently, the 'one-pot' synthesis of methyl benzenesulfinate has not achieved a good yield at temperature more than 60°C under microwave irradiation as well as conventional heating owing to the decomposition of reaction mixture. While the best yield was obtained at 94% after eight-hour stirring at room temperature (Fig. 1S, Supplementary) and at 90% after 30-minute ultrasonic irradiation (Fig. 2S, Supplementary). Thus, two activation methods, stirring at room temperature and ultrasonic irradiation, were selected for further experiments on the scope of thiols and alcohols.

Altogether four simple alcohols, *e.g.* methanol, ethanol, *n*-propyl alcohol, isopropyl alcohol and *n*-butanol were subjected to a tandem reaction of thiophenol or 4-methylthiophenol with *N*-bromosuccinimide by using two efficient methods. In the first series of tandem reactions, where the reactions were carried out under magnetic stirring at room temperature (Method A). The next series of reactions were performed as described in Method A (Experimental), but under the acceleration of ultrasonic irradiation (Method B). Summarily, the yields of the products were not remarkably different in both above methods, however the reaction time in Method B was reduced considerably (Table 2). The significant

**Table 2.** Yields of alkyl alkanesulfinates/arenesulfinates obtained by the tandem reaction of thiols, alcohols with NBS by various methods.[a]




**4 (a-p)**

| Entry | $R^1$ | $R^2$ | Product | Yield (%) (Time[b]) Method A[a] | Method B[a] |
|---|---|---|---|---|---|
| 1 | $C_6H_5$ | $CH_3$ | **4a** | 94 (8) | 90 (30) |
| 2 | $C_6H_5$ | $CH_3CH_2$ | **4b** | 79 (8) | 78 (40) |
| 3 | $C_6H_5$ | $CH_3CH_2CH_2$ | **4c** | 67 (8) | 65 (40) |
| 4 | $C_6H_5$ | $(CH_3)_2CH$ | **4d** | 69 (9) | 70 (40) |
| 5 | $C_6H_5$ | $CH_3(CH_2)_2CH_2$ | | 2 (8) | No trace |
| 6 | *p*-$CH_3C_6H_4$ | $CH_3$ | **4e** | 98 (8) | 91(30) |
| 7 | *p*-$CH_3C_6H_4$ | $CH_3CH_2$ | **4f** | 81 (8) | 80 (40) |
| 8 | *p*-$CH_3C_6H_4$ | $CH_3CH_2CH_2$ | **4g** | 69 (8) | 66 (40) |
| 9 | $C_6H_5CH_2$ | $CH_3$ | **4h** | 98 (8) | 96 (30) |
| 10 | *p*-$MeOC_6H_5$ | $CH_3$ | **4j** | 82 (8) | 86 (20) |
| 11 | *p*-$ClC_6H_4$ | $CH_3$ | **4k** | 74 (8) | 78 (30) |
| 12 | *n*-$C_4H_9$ | $CH_3$ | **4l** | 92 (8) | 94 (30) |
| 13 | *n*-$C_8H_{17}$ | $CH_3$ | **4m** | 83 (8) | 94 (30) |
| 14 | *c*-$C_6H_{11}$ | $CH_3$ | **4n** | 96 (8) | 97 (30) |
| 15 | $MeOC(O)CH_2$-$CH_2$ | $CH_3$ | **4p** | 94 (8) | 88 (20) |

[a]The reaction of thiol (3 mmol), alcohol (5 mL), NBS (6.0 mmol) dissolved in an additional alcohol (9 mL) and EtOAc (1 mL) was performed under magnetic stirring at room temperature (Method A) and ultrasound irradiation (Method B).
[b]Time = reaction time in hours for the method A; time = reaction time in minutes for the method B.

influence of ultrasound irradiation on the reaction time was dependent on the cavitation collapse to increase the interfacial contact area [46].

Further experiments showed that the structures of thiols did not influence considerably the reaction yields; while the longer carbon chains of alcohols were used, the lower yields of sulfinic esters were obtained, for instance, the yield of *n*-butyl benzenesulfinate was obtained either 2% after eight-hour magnetic stirring or 0% after 30-minute ultrasonic irradiation. Moreover, sulfinic esters have not appeared from the reaction of benzyl alcohol or phenol with thiophenol and NBS at optimized reaction condition. The analysis results reported by gas chromatography-mass spectrometry showed that the oxidation of benzyl alcohol into benzaldehyde (2%) by using *N*-bromosuccinimide occurred similarly to the previous literatures [47]. The aromatic substitution of bromine was not detected in the case of benzyl alcohol, however, it occurred at the *ortho* postion (2%) and the *para* position of phenol (12%). In addition, the formation and existence of disulfides were recognized in most optimized reaction conditions with the range of yields from 1% to 23%, particularly in case of phenylmethanethiol (Entry 9, Table 2). The long carbon chain of alcohols affected considerably to the presence of disulfide (18−23%) in the product mixture.

The introduced protocol for the synthesis of simple sulfinic esters offers many advantages in terms of high product yield, catalyst-free and shorter reaction time under mild and ultrasound-supported reaction conditions, compared to the reported methods in the different reaction conditions as well as catalysts (Table 3).

**Table 3.** Comparison of previous methods for direct synthesis of sulfinic ester from the reaction of thiols and alcohols.

| Catalyst/Reactant | Solvent | Condition | Time (h) | Yield (%) |
|---|---|---|---|---|
| CuI (5 mol%); 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) (10 mol%) | THF (1 mL, 0.5 M) | Stirred at 65°C under 1 atmosphere of oxygen | 18 | 56–91 [30] |
| Co/N-$SiO_2$-AC (1.46 mol%); $K_2CO_3$ (0.1 mmol) | excess alcohol | Stirred at 60–80°C under $O_2$ atmosphere | 24 | 45–91 [31] |
| Undivided cell with platinum electrodes and $nBu_4NBF_4$ (0.2 M) as the electrolyte | $CH_2Cl_2$ | Electrocatalyzed at room temperature under nitrogen atmosphere | 20 | 58–90 [32] |
| Eosin Y (2.0 mol%); green LEDS (2.50 W, $\lambda = 535$ nm) | excess alcohol | Photocatalyzed under air atmosphere | 0.5–2 | 51–90 [33] |
| *N*-Bromosuccinimide (2-3 eq) | alcohol:$CH_2Cl_2$ ($^V/_V = 1{:}1$) or excess alcohol | Stirred at 0°C or 25°C after NBS was added at 0°C | 1–15 | 42–98 [5, 39–40] |
| *N*-Bromosuccinimide (2 eq) | excess alcohol;EtOAc (1 mL) | Irradiated at room temperature in ultrasonic bath | 20–40 min | 65–97 [our work] |

## 3. Experimental

### 3.1. Instrumentation and chemicals

#### 3.1.1. Instrumentation

The reactions were carried out by means of a magnetic stirrer IKA Ret Basic C, speeding at 250 rpm and a BRANSON 1510 ultrasonic bath, operating at frequency 40 kHz with a power output of 70 W. The progress of the reaction was monitored by GC-FID Agilent 6890N apparatus equipped with capillary column (30 m × 320 $\mu$m × 0.25 $\mu$m), detector and injector temperature at 250°C. LC/MS analyses were performed on a micrOTOF-QII-ESI-Qq-TOF (Bruker Daltonics, D-28359 Bremen, Germany) with UV/VIS and MS detector, the heated capillary of iron trap mass spectrometer was set to 350°C, reverse column ACE 3C18 (5 µm × 4.6 × 150 mm) and ESI (electrospray ionization): µQTOF Bruker. NMR spectra were recorded on a Brüker Advance DPX 500 MHz spectrometer at 500 MHz ($^1$H) and 125 MHz ($^{13}$C).

#### 3.1.2. Chemicals

All commercially available chemicals used were from Aldrich and analyzed for authenticity and purity by GC/MS (gas chromatography/mass spectrometry) before being used.

### 3.2. Typical procedures

#### 3.2.1. The tandem reaction of thiols, alcohols with N-bromosuccinimide (4a-4p) under magnetic stirring (Method A) [2]

A solution of *N*-bromosuccinimide (6 mmol, 1.068 g) dissolved in simple alcohol (5 mL) and ethyl acetate (1 mL) was added slowly into the 25 mL two-neck round flask containing a solution of thiol (3 mmol) in simple alcohol (5 mL) and then 4 mL of alcohol was

added into the reaction mixture. The reaction mixture was stirred for eight hours at room temperature (Method A, Table 2). After the reaction completed, the reaction mixture was extracted with dichloromethane (4 × 10 mL). The combined extracts were neutralized by a saturated solution of sodium bicarbonate, washed with water until neutral (pH = 7) and dried by anhydrous $Na_2SO_4$. After the removal of the solvent by rotary evaporation, the remaining crude product was analyzed by GC-FID to control the reaction conversion and the product selectivity. The crude product was purified by column chromatography (silica gel 60, 0.04–0.06 mm, Scharlau, as static phase) using eluent as a mixture of *n*-hexane and ethyl acetate and identified the structure by HRMS and NMR spectroscopy.

#### 3.2.2. The tandem reaction of thiols, alcohols with N-bromosuccinimide (4a-4p) under ultrasonic irradiation (Method B)

A test tube (h = 20.0 cm, d = 3.0 cm) containing a pertinent quantity of thiol (3 mmol), *N*-bromosuccinimide (6 mmol, 1.068 g) dissolved in simple alcohol (14 mL) and ethyl acetate (1 mL) was placed into an ultrasonic bath and irradiated for the necessary period of reaction time (Method B, Table 2). After the reaction completed, the reaction mixture was worked up as in Method A.

### 3.3. Spectroscopic data

The structure elucidation of all products reported was measured by $^1$H NMR, $^{13}$C NMR and HRMS. The unknown NMR spectroscopic data are described below and well-known spectra of compounds (**4a** [32]; **4b, d-g** [22]; **4c, 4n** [41]; **4p** [48]; and **4j, 4k** [38,41] **4 l** [39,40]) have been found compatible with those reported in the literature.

**Methyl phenylmethanesulfinate** (**4 h**).

Hexane:ethyl acetate (9:1) $R_f$ = 0.53; colorless liquid, $^1$H NMR (500 MHz, $CDCl_3$) $\delta$(ppm) = 7.32-7.37 (m, 3H), 7.29 (d, $J$ = 7.5 Hz, 2H), 4.03 (d, $J$ = 13 Hz, 1H), 3.94 (d, $J$ = 13 Hz, 1H), 3.72 (s, 3H)[5]. $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$(ppm) = 130.50, 128.93 (2C), 128.89, 128.39, 64.16, 54.68. HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_8H_{10}O_2S$, 193.0294; found, 193.0334.

**Methyl 1-octanesulfinate** (**4 m**).

Hexane:ethyl acetate (9:1) $R_f$ = 0.62; colorless liquid, $^1$H NMR (500 MHz, $CDCl_3$) $\delta$(ppm) = 3.72 (s, 3H), 2.63-2.72 (m, 2H), 1.61-1.67 (m, 2H), 1.33-1.38 (m, 2H), 1.22-1.26 (m, 8H), 0.85 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$(ppm) = 57.07, 54.44, 31.83, 29.28, 29.08, 28.87, 22.70, 21.35, 14.15. HRMS-ESI: *m/z* $[M + Na]^+$ calcd for $C_9H_{20}O_2S$, 215.1076; found, 215.1089.

## 4. Conclusion

A direct synthesis from thiols and simple alcohols with *N*-bromosuccinimide to produce sulfinic esters has been developed under magnetic stirring and ultrasound irradiation. Ultrasound irradiation is regarded as green and remarkable accelerator for this transformation. Moreover, the utilization of heterogeneous and homogeneous acidic and base catalysts has illustrated their influences on the selectivity of reaction, in some cases the formation of disulfide in priority. Furthermore, the catalyst-free reactions of thiols and alcohols also get benefit from the addition of ethyl acetate as co-solvent in place of dichloromethane.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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