

## Research Article

# In Quest of “Stereoselective Switch” for On-Water Hydrothiolation of Terminal Alkynes Using Different Additives and Green Synthesis of Vicinal Dithioethers

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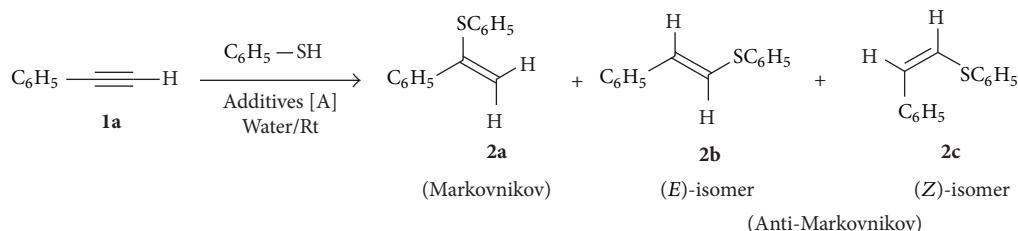
On-water hydrothiolation reaction between terminal alkyne and thiol has been probed in the presence of various additives. Aromatic alkynes yield corresponding 1-alkenyl sulfides, whereas aliphatic alkynes undergo double-addition yielding vicinal disulfides in good to excellent yields. Formation of 1-alkenyl sulfides proceeds with a high degree of regioselectivity (via anti-Markovnikov addition), and switching the stereoselectivity between *E/Z* isomers has been noticeably realized in the presence of different additives/promoters.

## 1. Introduction

Organosulfur compounds play a key role in biological processes, new materials, and chemical synthesis [1, 2]. 1-Alkenyl sulfides are important synthetic intermediates in total synthesis of many naturally occurring and biologically active compounds as well as versatile building blocks for many functionalized molecules [3–9]. The synthetic utility of alkenyl sulfides has been demonstrated in several reports by different research groups [10–17]. Increasing demand for alkenyl sulfides in material science, organic, and bioorganic chemistry has furthered the development of new synthetic methods [6, 18–21]. The addition of thiols to alkynes is considered as one of the straightforward methods to obtain vinyl sulphides either catalyzed by transition metal complexes [22–39], or base-promoted [40–44] and/or through free radicals [21, 45–48]. This reaction is often judged as a part of “click chemistry” and a process of high atom economy [49, 50]. Mechanistically, addition of thiols to alkynes is believed to occur (i) via radical pathway producing unselective mixture of (*E/Z*)-anti-Markovnikov vinyl sulphides, (ii) base-mediated nucleophilic addition giving all types of adducts, or (iii) transition-metal complex catalyzed processes yielding Markovnikov vinyl sulphides and (*E*) anti-Markovnikov vinyl

sulphides (Scheme 1). Varying degrees of stereo- and regioslectivity and turnover are reported in the literature [22–48].

Additives are a kind of reagents whose effects are very much similar to catalysts. They have often shown a profound role in variety of organic reactions in terms of the rate of the reaction, yield of the product, or change in the course of the reaction [51, 52]. In hydrothiolation, most reports in the literature described the formation of thermodynamically more stable *E*-vinyl sulfide in considerable excess over the *Z*-isomer. On the other hand, hydrothiolation, particularly of aryl and benzyl thiols and catalyzed by transition-metal complexes, often produces a mixture of anti-Markovnikov *E*-alkenyl sulfide (*syn* addition) and Markovnikov adduct and thus suffers from poor regioselectivity. Among the transition metal catalysts, rhodium complexes, both in homogeneous and heterogeneous forms, have exhibited high catalytic activity [51, 52]. Recently,  $\text{In}(\text{OTf})_3$  has been shown to selectively catalyze both Markovnikov and anti-Markovnikov hydrothiolation of terminal alkynes [38]. However, transition metal complexes are generally expensive, their uses are not ecofriendly, and the course of the reaction might suffer deactivation due to the formation of strong metal-sulphur bonds [53]. More regioselective (anti-Markovnikov) on-water hydrothiolation processes have been reported in



SCHEME 1: 1-Alkenyl sulphides from hydrothiolation of terminal alkynes.

the absence [45–48, 54] or presence of some additives like  $\beta$ -cyclodextrine [55]. Indeed, there are large varieties of reagents/catalysts that are used in the hydrothiolation of terminal alkynes with varying degrees of success in controlling stereo- and regioselectivity. However, many reports include expensive metal catalysts, nonaqueous solvents, and high temperature and moreover lack (*E/Z*)-stereoselectivity. In practice, there is no general guideline by which one can proceed to prepare a specific stereoisomer of a vinylic sulfide using this straightforward and atom-economic reaction under mild and environment-friendly conditions. Moreover, there are conditions that give rise to selective formation of the thermodynamically favoured (*E*)-alkenyl sulfide, it remains an unmet and elusive goal to develop optimum conditions that selectively produce (*Z*)-alkenyl sulfides under complete metal-free, base-free and on-water conditions. Since hydrothiolation of alkynes is a robust, atom-economic and highly useful synthetic method in C–S bond formation [6], we undertook a systematic investigation on the stereo- and regioselective addition of aliphatic and aromatic thiols to terminal alkynes in the presence of different additives in catalytic quantities under on-water conditions. We report herein our studies that constitute a rather broad guideline of “stereoselective switch” for the preparation of stereoselective (*E/Z*)-1-alkenyl sulfides.

## 2. Materials and Methods

All compounds were identified by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, recorded on a Bruker AV300 spectrometer operating at 300 and 75 MHz, respectively, and supported by FT-IR spectra. All NMR spectra were measured in chloroform-d. Chemical shifts are given in  $\delta$  (ppm) downfield from TMS. Analytical thin-layer chromatography (tlc) was performed on precoated aluminum plates from Merck silica gel 60 F<sub>254</sub> as the adsorbent (layer thickness 0.25 mm). The developed plates were air-dried and exposed to UV light. Column chromatography was performed on silica gel (source: SRL India; 60–120 mesh).

### 2.1. General Procedure for Monohydrothiolation of Alkynes.

To a mixture of alkyne (1 mmol), thiol (1.1 mmol) in water (0.5 mL) was added to the additive (1 mmol) and stirred at room temperature (25–30°C) for 2–5 h (TLC). The reaction mixture was extracted with diethyl ether ( $3 \times 10$  mL), and the combined organic layer was washed with brine and then dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of solvent under *vacuo* afforded an oily residue, which was passed through a short bed of silica

gel, and NMR spectrum was recorded to evaluate the percent of (*E/Z*) isomers. NMR spectral data and scanned copies of selected NMR spectra are given in the Supplementary Material available online at <http://dx.doi.org/10.1155/2014/358932> and are found to be in good agreement with those reported.

**2.2. General Procedure for Dihydrothiolation of Alkynes.** In a mixture of alkyne (1 mmol), thiol (2.2 mmol) in water (0.5 mL) was stirred for 5–9 h at room temperature (TLC). The reaction mixture was then extracted with diethyl ether (3 × 10 mL), and the combined organic layer was washed with brine and then dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of solvent under *vacuo* afforded an oily residue, which was passed through a short bed of silica gel to afford 1, 2-disulfides in good to excellent yields. The products were identified on the basis of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectral data, and/or by comparison with the data reported in the literature. NMR spectral data and scanned copies of selected NMR spectra ( $^1\text{H}$ - and  $^{13}\text{C}$ ) are given in the Supplementary Material.

### 3. Results and Discussion

Preliminary studies on the influence of catalyst and/or promoter on hydrothiolation were studied with a model reaction of phenyl acetylene (**1a**) and benzenethiol in the presence of various homogeneous and heterogeneous additives/promoters under on-water conditions at room temperature. Screening of additives/promoters included inorganic salts, water-soluble organic molecules, amino acids, surfactants, or heterogeneous ion-exchange resins, and the results are summarized in Table 1. Since the hydrothiolated adducts are formed in varying ratios (*E/Z* ratios), the results in Table 1 have been arranged showing a gradual change in the formation of (*E*)-vinyl sulfide (**2b**) to the (*Z*)-isomer (**2c**). The screening shows that the *E/Z* ratio in favor of (*E*)-vinyl sulfide (87:13) is formed in the presence of NaCl (Table 1, entry 3), while the major (*Z*)-vinyl sulfide is obtained in the presence of a combination of amberlite resins (Cl) and FeCl<sub>3</sub>·6H<sub>2</sub>O (entry 23; *E/Z* ratio 22:78). The stereochemical outcome favouring the (*E*)-isomer is also seen when the reaction is carried out at higher temperature (65°C) and continued for longer reaction time (10 h) (entry 11; *E/Z* ratio 88:12). However, a specific observation may be noted from this study that the on-water additions do not give rise to the formation of any Markovnikov adduct; that is, in no case was the other regioisomer (**2a**) obtained. The NMR spectral data

TABLE 1: Role of additives in the addition of PhSH to phenylacetylene under on-water conditions at room temperature producing selectively anti-Markovnikov adducts<sup>a</sup>.

|                 |                                    | $\text{C}_6\text{H}_5 - \text{C}\equiv\text{C} - \text{H} \xrightarrow[\text{Water/Rt}]{\text{Additives [A]}} \begin{array}{c} \text{H} \\   \\ \text{C}_6\text{H}_5 - \text{C} = \text{C} - \text{SC}_6\text{H}_5 \\   \\ \text{H} \end{array} + \begin{array}{c} \text{C}_6\text{H}_5 \\   \\ \text{H} - \text{C} = \text{C} - \text{SC}_6\text{H}_5 \\   \\ \text{H} \end{array}$ |       |  |                            |
|-----------------|------------------------------------|--|-------|--|----------------------------|
| Entry           | Additive [A] <sup>b</sup>          | (E/Z) ratio <sup>c,d</sup>   | Entry | Additive [A] <sup>b</sup>                                      | (E/Z) ratio <sup>c,d</sup> |
| 1               | Nil (neat)                         | 83:17  | 13    | CuI-Catechol violet  | 60:40                      |
| 2               | Nil (water)                        | 80:20  | 14    | Amberlite resins (Cl)  | 58:42                      |
| 3               | NaCl                               | 87:13  | 15    | n-Bu <sub>4</sub> NBr  | 57:43                      |
| 4               | Sucrose                            | 85:15  | 16    | D-Glucose  | 56:44                      |
| 5               | CF <sub>3</sub> COOH               | 78:22  | 17    | CuI  | 52:48                      |
| 6               | BF <sub>3</sub> ·Et <sub>2</sub> O | 76:24  | 18    | Cholesterol  | 51:49                      |
| 7               | Catechol violet                    | 75:25  | 19    | CTAB   | 49:51                      |
| 8               | L-Proline                          | 70:30  | 20    | FeCl <sub>3</sub> ·6H <sub>2</sub> O                           | 44:56                      |
| 9               | Glycin                             | 69:31  | 21    | Amberlyst resins (OH)  | 40:60                      |
| 10              | Starch                             | 64:36  | 22    | D-Glucose and FeCl <sub>3</sub> ·6H <sub>2</sub> O             | 35:65                      |
| 11 <sup>e</sup> | Water (65°C)                       | 88:12  | 23    | Amberlite resins (Cl) and FeCl <sub>3</sub> ·6H <sub>2</sub> O | 22:78                      |
| 12              | Water (65°C)                       | 64:36  |       |  |                            |

<sup>a</sup>Reaction conditions: phenyl acetylene (0.5 mmol), PhSH (0.55 mmol), water (1 mL), 2 h. <sup>b</sup>Additive [A] (2 mol %). <sup>c</sup>E/Z ratio was determined by <sup>1</sup>H NMR of the crude mixture. <sup>d</sup>Yield of the mixture of stereoisomers after chromatographic purification varies in the range 80–90%. <sup>e</sup>The reaction was continued for 10 h; all other reactions were carried out at room temperature unless otherwise mentioned.

of the unpurified products indicated only a mixture of **2b** and **2c**, and indeed there was no trace of **2a**.

At this point, effect of functional groups in the aromatic moiety in either of the addition partners could be worth investigating. Since a combination of ion-exchange resins and ferric chloride showed a better selectivity towards the formation of (*Z*)-vinyl sulfide, this study was performed under similar conditions. The results are presented in Table 2. It is seen that both electron-donating and electron-withdrawing functional groups present on the aryl ring can give rise to the anti-Markovnikov hydrothiolation products in excellent yields (85–94%). The highest (*Z*)-selectivity was found in the reaction between phenyl acetylene and *p*-methoxybenzenethiol (Table 2, entry 4; E/Z 12:88), possibly due to the easy emulsification of the alkyne in water upon stirring, which might be supportive, in addition to the presence of the additive. On the other hand, presence of the electron-withdrawing group (fluorine) on the thiol part did not show any appreciable influence towards stereoselective addition yielding the (*E*)-isomer in major quantity (entries 6–7). It seems that there is not much electronic influence of the functional groups in the aryl ring of either of the addition partners; rather their stability in water in the presence of the additive might have some control towards anti-Markovnikov stereoselectivity.

Further studies of aryl acetylenes (terminal) with aliphatic thiols in the presence of one equivalent of D (+)-glucose showed a general trend in favour of the formation of (*Z*)-vinyl sulphides. For example, phenyl acetylene or *p*-tolyl acetylene undergoes hydrothiolation in the presence of *n*-alkyl thiols that afforded the corresponding 1-alkenyl sulphides with (E/Z) ratios (14:86). The results are summarized in Table 3.

Since there is significant reactivity difference between aliphatic and aromatic thiols [56, 57], we ought to investigate the stereochemical outcome in two other cases: hydrothiolation of (i) aliphatic terminal alkynes and aliphatic thiols and (ii) aliphatic terminal alkynes and aromatic thiols. It has been seen from previous reports that aliphatic alkynes undergo dihydrothiolation yielding *vicinal* disulfides only irrespective of the nature of the thiol [45, 54]. Thus, aliphatic terminal alkynes were subjected to hydrothiolation with aromatic and aliphatic thiols under on-water conditions. Seemingly, there was an influence of additives on this double-addition reaction. The results are presented in Table 4, which show that aliphatic terminal alkynes undergo double- additions yielding finally 1, 2-disulfides only in the presence or absence of D (+)-glucose.

With regard to the mechanism of hydrothiolation of terminal alkynes in water, the literature reports are of different views. For example, Bhadra and Ranu [54], in their studies on water-promoted regioselective hydrothiolation, ruled out the likeliness of a radical pathway as the reaction proceeds in the presence of dissolved oxygen. On the other hand, Jin et al. [45], hinted that the reaction probably proceeds through a radical mechanism under similar conditions. The latter group further observed that the reaction does not occur in the presence of galvinoxyl-free radical, although use of such radical quencher does not always prove radical mechanism [54, 55]. Our studies indeed demonstrated a role of additives in governing the stereoselectivity but the specific function of the additive, particularly in aqueous medium, and the mechanistic routes are not clear at this time. Furthermore, carrying out the reaction in the presence of radical initiator (AIBN) or light did not make the process faster appreciably. Several transition metal complexes are

TABLE 2: Hydrothiolation of aryl thiol [B] to aryl acetylene [A] in (1.1:1) in water at room temperature.

| Entry | [A]  | [B]   |          | Amberlite resins (Cl)<br>-FeCl <sub>3</sub> /water/r.t. | [C]                  |  |
|-------|--|---|----------|---|----------------------|--|
|       | R <sup>1</sup> -C <sub>6</sub> H <sub>4</sub> -C≡H | R <sup>2</sup> -C <sub>6</sub> H <sub>4</sub> -SH | Time (h) | Yield <sup>a</sup> (%) [C]                              | E/Z [C] <sup>b</sup> |  |
| 1     | R <sup>1</sup> = H                                 | R <sup>2</sup> = H                                | 2.0      | 85  | 22:78                |  |
| 2     | R <sup>1</sup> = CH <sub>3</sub>                   | R <sup>2</sup> = H                                | 3.5      | 91  | 40:60                |  |
| 3     | R <sup>1</sup> = CH <sub>3</sub>                   | R <sup>1</sup> = CH <sub>3</sub>                  | 2.5      | 88  | 29:71                |  |
| 4     | R <sup>1</sup> = H                                 | R <sup>1</sup> = OCH <sub>3</sub>                 | 3.0      | 93  | 12:88                |  |
| 5     | R <sup>1</sup> = CH <sub>3</sub>                   | R <sup>1</sup> = OCH <sub>3</sub>                 | 2.0      | 90  | 22:78                |  |
| 6     | R <sup>1</sup> = H                                 | R <sup>2</sup> = F                                | 2.0      | 88  | 80:20                |  |
| 7     | R <sup>1</sup> = CH <sub>3</sub>                   | R <sup>2</sup> = F                                | 2.0      | 94  | 39:61                |  |

<sup>a</sup>Yield represents the product [C] after purification by column chromatography. <sup>b</sup>E/Z ratio was determined by <sup>1</sup>H NMR of the crude mixture.

TABLE 3: Hydrothiolation aromatic terminal alkynes with aliphatic thiols.

| Entry | [A]  | [B]                                 |          | D (+)-glucose<br>/water/r.t. | [C]                  |  |
|-------|--|-------------------------------------|----------|------------------------------|----------------------|--|
|       | R <sup>1</sup> -C <sub>6</sub> H <sub>4</sub> -C≡H | (CH <sub>2</sub> ) <sub>n</sub> -SH | Time (h) | Yield <sup>a</sup> (%) [C]   | E/Z [C] <sup>b</sup> |  |
| 1     | R <sup>1</sup> = H                                 | n = 3                               | 3.0      | 75                           | 20:80                |  |
| 2     | R <sup>1</sup> = H                                 | n = 5                               | 3.0      | 64                           | 14:86                |  |
| 3     | R <sup>1</sup> = CH <sub>3</sub>                   | n = 3                               | 4.5      | 79                           | 14:86                |  |
| 4     | R <sup>1</sup> = CH <sub>3</sub>                   | n = 5                               | 5.0      | 51                           | 21:79                |  |

<sup>a</sup>Yield represents the product [C] after purification by column chromatography. <sup>b</sup>E/Z ratio was determined by <sup>1</sup>H NMR of the crude product mixture.

TABLE 4: Dihydrothiolation of aliphatic alkyne with thiols in water at room temperature.

| Entry          | [A]  | [B]  |            | [C]   |    |
|----------------|--|--|------------|---|----|
|                | R <sup>1</sup> -C≡H  | R <sup>2</sup> -SH   | Water/r.t. | R <sup>2</sup> S-C(R <sup>1</sup> ) <sub>2</sub> -SR <sup>2</sup> |    |
| 1 <sup>c</sup> | R <sup>1</sup> = CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> | R <sup>2</sup> = Ph  |            |   | 88 |
| 2              | R <sup>1</sup> = CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> | R <sup>2</sup> = Ph  |            |   | 76 |
| 3              | R <sup>1</sup> = CH <sub>2</sub> OAc                               | R <sup>2</sup> = Ph  |            |   | 79 |
| 4              | R <sup>1</sup> = CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> | R <sup>2</sup> = CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> |            |   | 58 |

<sup>a</sup>[A]:[B] is 1:2.2. <sup>b</sup>Yield represents the product [C] after purification by column chromatography. <sup>c</sup>D (+)-Glucose (1 equiv) was added.

known to catalyze the process of hydrothiolation via radical intermediates leading to major anti-Markovnikov 1-alkenyl sulfides. In the absence of such metal complexes, it seems that stabilization of the reactive species by water as well as by the additive might govern the course of the reaction as well as the stereoselectivity.

#### 4. Conclusions

In quest of finding “stereoselective switch” for the hydrothiolation of terminal alkynes under on-water conditions, our studies apparently revealed two types of additives that could

lead to the stereoselective formation of the (Z)-1-alkenyl sulfides in substantial quantities depending on the nature of both reacting partners. Since most of the metal-free methods describe formation of the (E)-1-alkenyl sulfides in major amount, the present findings could steer in designing mild and green reaction conditions for stereoselective preparation of (E/Z) alkenyl sulphides under on-water conditions.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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