A sustainable process for gram-scale synthesis of stereoselective aryl substituted (*E*)-2-thiocyanatoacrylic acids

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Abstract. We have developed a new, simple and sustainable process for stereoselective synthesis of aryl substituted (*E*)-2-thiocyanatoacrylic acids by nucleophilic substitution and Knoevenagel condensation involving chloroacetic acid, ammonium thiocyanate and aromatic aldehydes at room temperature. The selectivity was controlled by appropriately choosing aromatic aldehydes. The influence of intramolecular hydrogen bonding of 3-(2-hydroxyphenyl)-2-thiocyanatoacrylic acid involves the formation (*Z*) isomers. The salient features of the present protocol are mild reaction conditions, excellent yield, easy filtration, clean reaction profiles and applicability towards gram-scale synthesis. Importantly, the synthetic application of this protocol leads to the emergence of various biologically important compounds.

Keywords. (*E*)-2-thiocyanatoacrylic acids; Knoevenagel condensation; stereoselective synthesis; gram-scale synthesis.

1. Introduction

The formation of carbon-sulfur bond constitutes a key reaction in biosynthetic processes as well as in organic synthesis.¹ Sulfur-containing molecules are ranked top among the most imperative motifs in natural and biologically important compounds (Figure 1).^{2–8} Due to the development of milder and safer access to the thiocyanates, it is obvious that a larger scientific community will be attracted by this multitasking functional group. Particularly, these species act as the building blocks for many heterocyclic or organosulfur compounds.⁹ For example, thiocyanates are used as precursors to other sulfur-based functional groups such as thiols, thioethers, disulfides, isothiocyanates and phosphonothioates. In addition, thiocyanates act as pseudohalides and cyanating agents. They show a wide range of biological activities such as anticancer agents,¹⁰ antioxidants,¹¹ pro-inflammatory activity,¹² anti-inflammatory and anti-microbial effects.¹³ This functional group serves as a precursor to the preparation of many pharmaceutical compounds including agrochemicals, drugs and dyes.^{14–16} Furthermore, thiocyanates can readily be

transformed into a more versatile sulfur-bearing group for the additional structure modification.^{17–20}

Acrylic acid derivatives are key intermediates for the synthesis of various biologically important compounds.²¹ Generally, aryl acrylic acids and their amides have potent inhibitory activity as well as good antioxidant and anti-inflammatory activities.²² Due to their great importance, development of a novel synthetic approach for the preparation of aryl substituted -2-thiocyanatoacrylic acid derivatives is attempted herein. A new synthetic route for this valuable scaffold is reported *via* nucleophilic substitution (C-S bond formation) and Knoevenagel condensation (C-C bond formation). Generally, the Knoevenagel condensation of aldehydes with an active methylene compound is one of the classical methods for carbon-carbon²³ bond formation in organic synthesis.

Since 1898, Knoevenagel condensation has been showing several advantages like reaction simplicity, mild conditions, and application in synthesizing biologically privileged compounds which have made it an active field of research among organic chemists.²⁴ Commonly, many researchers have used Knoevenagel condensation by involving various aldehydes with different active methylene compounds such as Meldrum's

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Figure 1. Bioactive thiocyanate-containing natural products.

acid, dimedone, barbituric acid, malononitrile, cyanoacetamide, acetylacetone, ethylacetoacetate, ethyl cyanoacetate and cyanoacetic acid (Figure 2a–i).^{25–31} While all these types of active methylene compounds provide access to Knoevenagel products, there are certain limitations associated with them such as the use of hazardous bases, harsh reaction conditions, tedious workup procedures and selectivity. Therefore, we aim to develop a mild, efficient and selectivity-controlled approach with new active methylene compound to produce highly desired Knoevenagel products. In the present study, we describe the development of a practical process for the gram-scale synthesis of stereoselective aryl substituted (E)-2-thiocyanatoacrylic acids involving chloroacetic acid, ammonium thiocyanate, aromatic aldehydes and ammonium acetate at room temperature (Scheme 1).

Notably, in this newly developed protocol, NH_4SCN acts as a source of $-\text{SCN}$ and is used to combine with chloroacetic acid to make a new compound containing active methylene group (2-thiocyanatoacetic acid). This gram-scale synthetic process will certainly be highly beneficial for industrial purposes and practical process in the organic laboratory.

2. Experimental

2.1 Materials and physical measurements

All the chemicals are commercially available and purchased from Sigma-Aldrich or Merck and used as received. The ^1H ,

^{13}C NMR spectra were recorded on a Bruker (Avance) 400 and 500 MHz NMR instrument using $\text{DMSO}-d_6$ as solvent. The standard Bruker software was used throughout. Chemical shifts are reported in parts per million (ppm, δ units) and coupling constants are given in hertz. Thin layer chromatography (TLC) was run on the silica gel-coated aluminium sheets and glass plates (silica gel 60 GF254, E. Merck, Germany) and visualized in iodine chamber and confirmed under UV light (254 nm). ESI-HRMS spectra were recorded on Bruker Maxis 10138 mass spectrometer.

2.2 General procedure for compound 2

A mixture of chloroacetic acid (1.5 equiv.) and ammonium thiocyanate (1.5 equiv.) in 5/5 mL of acetonitrile/methanol were taken and stirred well for 15 min at room temperature. Then, aromatic aldehyde (1 equiv.) and ammonium acetate (1.5 equiv.) were added to the reaction mixture and this reaction was continued for 12 h. After completion of the reaction, it was monitored in TLC and then the reaction mixture was poured into the 400 mL cold water. The formed precipitate of products were filtered by simple filtration and washed with water to obtain the crude product. The crude product was recrystallized by using absolute ethanol to get pure product 2.

3. Results and Discussion

We began initially the reaction of chloroacetic acid, NH_4SCN and aldehyde 1 in CH_3CN at room temperature. The reaction mixture in the absence of a base did not yield the desired product 2 and only thiocyanation reaction took place with the yield of 98% of 2-thiocyanatoacetic acid (3) (Table 1, entry 1).

Figure 2. Different active methylene groups involved in the formation Knoevenagel products.

Scheme 1. Synthetic route for the 2-thiocyanatoacrylic acid derivatives **2**.

Then the active methylene protons of **3** got activated when the reaction mixture under a basic condition with several organic and inorganic bases were investigated. Among the organic bases, Et_3N produced a moderate yield of desired product **2** (58%, Table 1, entry

2). Whereas inorganic bases like NH_3 and NH_4OAc improved the yield of the desired product **2**, respectively, to 67% and 75% (Table 1, entries 2 and 3), yet these conversions were unsatisfactory. Next, various solvents such as THF, EtOH and MeOH were tested and screened for the desired product **2** (Table 1, entry 4–6). Finally, the synthesis of aryl substituted 2-thiocyanatoacrylic acid derivative reactions could be achieved efficiently at room temperature with an excellent yield (99%, Table 1, entry 8) in mixed solvents such as CH_3CN -MeOH (v/v = 1:1).

Table 2 shows the formation of selectivity-controlled products of *E*-isomers of 2-thiocyanatoacrylic acid

Table 1. Optimization of the reaction conditions for the synthesis of aryl substituted 2-thiocyanatoacrylic acid derivatives.

Entry	Base	Time (h)	Solvent	Yield 2a (%)
1	- ^b	12	CH ₃ CN	-, (98% of 3) ^c
2	Et ₃ N	12	CH ₃ CN	58
3	NH ₃	12	CH ₃ CN	67
4	NH ₄ OAc	12	CH ₃ CN	75
5	NH ₄ OAc	12	THF	80
6	NH ₄ OAc	12	EtOH	78
7	NH ₄ OAc	12	MeOH	85
8	NH ₄ OAc	12	CH ₃ CN/MeOH ^d	99 ^e

^aReaction conditions: chloroacetic acid, ammoniumthiocyanate and aromatic aldehyde at room temperature for 12 h. ^bwithout base. ^conly active methylene compound **3** formation.

^dmixture of solvents. ^eexcellent conversion yield.

Table 2. Selectivity controlled synthesis of aryl substituted-2-thiocyanatoacrylic acids from appropriately chosen aromatic aldehydes.

Entry	R ^a	Time (h)	2 ^b (<i>E</i>)-isomer (%)	2 (<i>Z</i>)-isomer (%)
1	H (1a)	12	98	- ^c
2	4-OCH ₃ (1b)	12	98	- ^c
3	4-CH ₃ (1c)	12	97	- ^c
4	4-Cl (1d)	12	96	- ^c
5	4-OH (1e)	12	95	- ^c
6	3-Br (1f)	12	92	- ^c
7	3,4-di-OCH ₃ (1g)	12	98	- ^c
8	3,4,5-tri-OCH ₃ (1h)	12	99	- ^c
9	Furfuraldehyde (1i)	12	98	- ^c
10	Thiophenealdehyde (1j)	12	99	- ^c
11	4-(diphenylamino)benzaldehyde (1k)	12	96	- ^c
12	2-OH (1l)	12	53	45 ^d
13	Crotonaldehyde	12		Trace

^aPosition of substitution on the ring; ^bsuccessful formation of (*E*)-isomer; ^cno formation of (*Z*) isomer;

^dformation of (*Z*)-isomer.

Figure 3. Photographic image of (*E*)- and (*Z*)-3-(2-hydroxyphenyl)-2-thiocyanatoacrylic acid isomers on TLC (25% ethyl acetate with hexane elution).

derivatives from chloroacetic acid, NH_4SCN , aromatic aldehydes in the presence of NH_4OAc in CH_3CN - MeOH mixture solvent. Firstly, un-substituted aromatic

aldehyde was examined. Benzaldehyde (**1a**) gave an excellent yield of *E*-isomer (Table 2, entry 1). Among the various substituted aldehydes tested, 4-substituted aldehydes (**1b–1e**) produced almost 95–98% yield of the desired *E*-isomer, **2b–e** (Table 2, entry 2–5). 3-bromo substituted benzaldehyde (**1f**), 3,4-di- (**1g**) and 3,4,5-trimethoxy substituted benzaldehyde (**1h**) were also found to produce good yields of *E*-isomer (Table 2, entries 6–8). Similarly, the hetero aromatic aldehydes (**1i** and **1j**) gave higher yields of *E*-isomer (Table 2, entry 9 and 10). 4-(diphenylamino)benzaldehyde (**1k**) was tested and gave 96% of (*E*)-2-thiocyanatoacrylic acid (Table 2, entry 11). But both (*E*) & (*Z*) isomers were obtained from 2-hydroxy benzaldehyde (**1l**) (Table 2, entry 12). Then an aliphatic unsaturated aldehyde (crotonaldehyde (**1m**)) was also tested but only a trace amount of yield was obtained (Table 2, entry 13). The formation of both *E* and *Z* isomers may be attributed to the influence of intramolecular hydrogen bonding.³² The (*E*)- & (*Z*)-3-(2-hydroxyphenyl)-2-thiocyanatoacrylic acid (**2i**) isomers were easily separated out which could be visualized by naked eye through TLC (Figure 3).

Figure 4. ^1H -NMR ($\text{DMSO}-d_6$) Spectra. (a) *E*-isomer and (b) *Z*-isomer of 3-(2-hydroxyphenyl)-2-thiocyanatoacrylic acid showing intramolecular hydrogen bonding effect.

Figure 5. Selectivity controlled synthesis of aryl substituted (*E*)-2-thiocyanatoacrylic acids.

Further, the isomers were separated individually by column chromatography (eluant hexane: ethyl acetate) and the intramolecular hydrogen bonding was identified with peaks shifts from low to high region in $^1\text{H-NMR}$ spectrum of (*E*) & (*Z*) isomers which was indicated by the difference of $-\text{OH}$ (0.08 ppm) and $-\text{COOH}$ (0.01 ppm) peaks as shown in Figure 4. The substituted aldehydes (**1a–1k**) formed only the (*E*)-2-thiocyanatoacrylic acids which was confirmed by (in addition to NMR analysis (vide *ESI*)) TLC plates showing only one spot (figure not shown) when compared to 2-hydroxy benzaldehyde (**1l**) (Figure 3).

From the Figure 5, it can be clearly seen that the selectivity could be achieved in the formation of aryl substituted 2-thiocyanatoacrylic acids by proper selection of aromatic aldehydes, *viz* unsubstituted, 4-substituted, 3-substituted, 3,4-disubstituted and 3,4,5-tri substituted which give only *E*-isomers (Figure 5a–k). But 2-OH benzaldehyde gives both the isomeric products (*E* & *Z*) due to the intramolecular hydrogen bonding (Figure 5 l).

With the optimized conditions in hand (Table 1, entry 8), the substrate scope of the present study with respect to various aromatic and hetero aromatic aldehydes were evaluated and the results are summarized in Scheme 2. Both electron donating groups (EDGs) and electron withdrawing groups (EWGs) on phenyl rings of the aldehydes give the corresponding desired aryl substituted (*E*)-2-thiocyanatoacrylic acids (Scheme 2, **2a–2h**) in good yields. In the case of five membered

heterocyclic aldehydes such as furfuraldehyde and thiophenealdehyde, the products were obtained in 98% and 99% yields respectively (Scheme 2, **2i** and **2j**). Furthermore, 4-(diphenylamino)benzaldehyde effectively react under the optimized reaction conditions and give the corresponding (*E*)-2-thiocyanatoacrylic acids **2k** in 96% yield. But, hydroxyl group in the second position on benzaldehyde generates the (*E*) & (*Z*)-2-thiocyanatoacrylic acids (**2l**) with 45 and 58% yields, respectively.

We then extended the work for the gram-scale synthesis of **2h** under the optimized conditions. Pleasingly, (*E*)-2-thiocyanato-3-(3,4,5-trimethoxyphenyl) acrylic acid (**2h**) was obtained in an excellent yield (99%) which was conducted on a gram scale process (Figure S1 in Supplementary Information), which indicates that there is a potential for practical methods in organic laboratory and industrial applications too.

The plausible mechanism for the formation of aryl substituted 2-thiocyanatoacrylic acid is depicted in Scheme 3. First, the nucleophilic substitution reaction of thiocyanate ion (SCN^-) with the α -carbon of chloroacetic acid takes place to form a 2-thiocyanatoacetic acid, **3**. Then, **3** interacts with ammonium acetate to produce the ammonium 2-thiocyanatoacetate salt **4** which was activated by ammonium acetate abstracting a proton from the methylene group of **4**. Then, **4** undergoes Knoevenagel condensation with protonated aldehyde to form **5** which was neutralized by water to afford the product **2**.

Scheme 2. Synthesis of aryl substituted (*E*)-2-thiocyanatoacrylic acids **2**.

Scheme 3. Plausible mechanism for the synthesis of (*E*)- and (*Z*)-2-thiocyanatoacrylic acids.

4. Conclusions

In summary, we have achieved a novel, mild and efficient method for the selective synthesis of aryl substituted (*E*)-2-thiocyanatoacrylic acids from easily available starting materials in very good yields. The selectivity was controlled by the selection of appropriate aromatic aldehydes. Furthermore, the advantages of this method are the selectivity control, mild reaction conditions, excellent yields, operational simplicity, absence of tedious separation procedures, easy handling, clean reaction profiles and energy efficiency. The current methodology with mild reaction conditions and operational simplicity offers a method for gram-scale synthesis and applicability to practical processes in organic laboratory and industry.

Supplementary Information (SI)

The spectral data and copies of ^1H , ^{13}C NMR and HRMS of all the compounds are given in the Supplementary Information which is available at www.ias.ac.in/chemsci.

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