# A New Route to Allyl Thiols and Allyl Thiocarbamates from Baylis-Hillman Adducts



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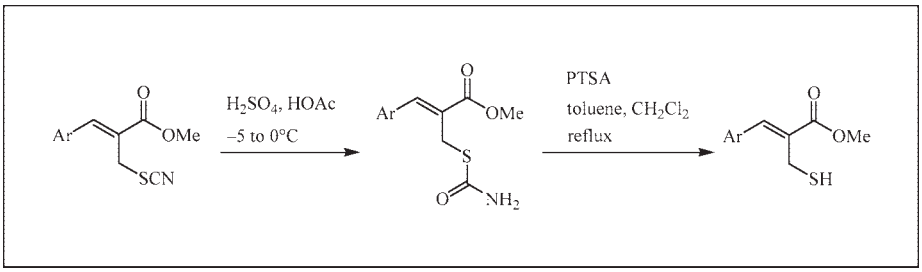


A facile synthesis of trisubstituted allyl thiols and allyl thiocarbamates has been accomplished from Baylis-Hillman adducts through bromination, thiocyanation, and acid-assisted hydrolysis reaction.

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## INTRODUCTION

Thiols have attained significant importance as synthetic intermediates for valuable sulfur-containing compounds [1]. A number of reports have appeared on the potential applications of thiol functionality in various scientific disciplines such as pharmaceutical chemistry [2], self-assembled monolayers [3], nanoparticles [4], and conducting polymers [5]. Also, *S*-alkyl thiocarbamates are an important class of compounds that have received considerable attention [6,7] because of their numerous biological effects including anesthetic [8], fungicidal [9], bactericidal [9,10], pesticidal [11,12], and antiviral [13]. Despite the aforementioned reasons, thiocarbamates are most noted for their use as commercial herbicides [14].

Generally, thiols have been synthesized mainly from alkyl halides with thioacetate ion followed by deacetylation with base [15], disulfides *via* reduction [16], alkenes *via* anti-Markovnikov addition of thiolacetic acid, followed by deacetylation with strong base [17], alcohols *via* refluxing with hydrobromic acid and thiourea, followed by hydrolysis with strong base [18], thiocyanates *via* reduction [19], and thiocarbamates *via* hydrolysis [20]. The most widely used method for the preparation of thiocarbamates makes use of gaseous carbonyl sulfides and an amine, followed by subsequent treatment with base and alkyl halide [12,21], condensation of a thiol with an isocyanate [10], nucleophilic substitution of trichloroacetyl chloride with a thiol, followed by treatment of an amine [22], and the hydration of an organic thiocyanate [23,24]. In view of their significance in organic synthesis, it is still necessary to extend the scope of the allyl thiol and thiocarbamate families and develop new and convenient synthetic routes. Here the Baylis-Hillman (BH) chemistry [25] has been applied for the synthesis of these compounds.

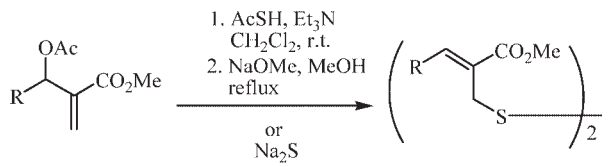
## RESULTS AND DISCUSSION

The BH reaction is well known as a powerful carbon–carbon bond forming methods in organic synthesis [26]. Nucleophilic displacement of BH acetates or bromides is an important protocol for the synthesis of trisubstituted alkenes. Although there exist several methods for the nucleophilic displacement of BH acetates or bromides with various reagents [27], displacement with sulfur nucleophiles is limited [28].

Recently, we reported substitution reaction of BH acetates **1** with thiolacetic acid followed by deacetylation with base [29], and with sodium sulfide [30] to give the symmetric diallyl disulfides **2**, respectively, as shown in Scheme 1. No traces of the intended allyl thiols were produced. Although the literature has reported some interesting schemes to obtain allyl thiols, we felt that thiols can be obtained from allyl thiocyanates.

The known allyl thiocyanates **4** were obtained in high yields by displacement of 2-(bromomethyl)alkenoates with sodium thiocyanate [31], derived from BH adducts with *N*-bromosuccinimide-dimethyl sulfide [32]. Treatment of allyl thiocyanates **4** with 95% sulfuric acid–acetic acid (9:1, v/v) at −5 to 0°C produced allyl thiocarbamates **5** in 54–96% yields. On hydrolysis reaction of **5**

**Scheme 1**




**1** **2**

with one equivalent of *p*-toluenesulfonic acid monohydrate (PTSA) in toluene and dichloromethane (9:1, v/v) reflux temperature, allyl thiols **6** were obtained in 75–94% yields (Scheme 2, Table 1). When using 0.1 equivalent of PTSA, the reaction was sluggish and the yield was low (Entries 1, 2, 7). Direct one-pot transformation of thiocyanate **4** to thiol **6** was unsuccessful with PTSA in refluxing toluene. All the products are unambiguously characterized using infrared spectra, $^1$H and $^{13}$C NMR data. In the $^1$H NMR spectra, the characteristic chemical shift of the thiol protons of **6** were found at $\delta = 2.05$–2.12 as a triplet ($J = 7.6$–8.3 Hz), the methylene protons were observed at $\delta = 3.33$–3.60 as a doublet ($J = 7.6$–8.3 Hz), and the methine protons resonated at $\delta = 7.63$–7.92 as a singlet. Their infrared spectra showed absorption at 2557–2593 cm$^{-1}$ for the thiol band.

## CONCLUSION

In conclusion, a new method for the synthesis of trisubstituted allyl thiols from BH adducts has been developed through bromination, thiocyanation, and acid-assisted hydrolysis reaction.

## EXPERIMENTAL

Silica gel 60 (70–230 mesh ASTM) used for column chromatography was supplied by E. Merck. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 $F_{254}$ TLC plates. Melting points were measured by an Electrothermal melting point apparatus and were uncorrected. Microanalysis was obtained using a Thermo Electron Corporation Flash EA 1112 element analyzer. Infrared spectra were recorded with a Nicolet Magna 550 FTIR spectrometer. The $^1$H and $^{13}$C NMR spectra were measured on a Gemini 300 spectrometer using deuteriochloroform. All chemical shifts are reported in parts per million relative to tetramethylsilane. The coupling constants ($J$) are expressed in Hertz.

The known methyl 3-aryl-2-(thiocyanatomethyl)propenoates **4** were prepared according to the literature procedure [31].

**General procedure for the preparation of methyl (*Z*)-3-aryl-2-(carbamoylthiomethyl)propenoates 5.** To an ice-cold mixture of 95% sulfuric acid (9 mL) and acetic acid (1 mL), allyl thiocyanate **4** (2 mmoles) was added in small portions for 15 min under stirring at −5 to 0°C. After dissolution of **4**, the mixture was stirred at room temperature for 0.5–2.5 h and then poured onto crushed ice. The white precipitate was collected by suction filtration, dried, and crystallized from dichloromethane and petroleum ether to give compound **5**.

The physical and spectral data of **5** prepared by this general method are as follows.

***Methyl (Z)-2-carbamoylthiomethyl-3-phenylpropenoate (5a).*** Reaction time: 1 h; white solid; yield: 75%; mp: 99–100°C; ir (potassium bromide): 3419, 3327, 3182, 1707, 1675, 1597 cm$^{-1}$; $^1$H NMR (deuteriochloroform): δ 3.85 (s, 3 H, $OCH_3$), 4.11 (s, 2 H, $CH_2$), 5.58 (s, 2 H, $NH_2$), 7.37–7.47 (m, 5 H, aromatic), 7.82 (s, 1 H, CH); $^{13}$C NMR (deuteriochloroform): δ 27.8, 52.4, 127.1, 128.7, 129.3, 129.5, 134.4, 142.5, 167.6, 168.4. *Anal*. Calcd. for $C_{12}H_{13}NO_3S$: C, 57.35; H, 5.21; N, 5.57; S, 12.76. Found: C, 57.20; H, 5.07; N, 5.39; S, 12.53.

***Methyl (Z)-2-carbamoylthiomethyl-3-(4-chlorophenyl)propenoate (5b).*** Reaction time: 1 h; white solid; yield: 84%; mp: 108–109°C; ir (potassium bromide): 3396, 3298, 3202, 1707, 1655, 1619, 1592 cm$^{-1}$; $^1$H NMR (deuteriochloroform): δ 3.85 (s, 3 H, $OCH_3$), 4.07 (s, 2 H, $CH_2$), 5.50 (s, 2 H, $NH_2$), 7.40 (s, 4 H, aromatic), 7.75 (s, 1 H, CH); $^{13}$C NMR (deuteriochloroform): δ 27.7, 52.4, 127.7, 129.0, 130.9, 132.8, 135.3, 141.0, 167.4, 168.2. *Anal*. Calcd. for $C_{12}H_{12}ClNO_3S$: C, 50.44; H, 4.23; N, 4.90; S, 11.22. Found: C, 50.19; H, 4.08; N, 5.20; S, 10.96.

**Scheme 2**

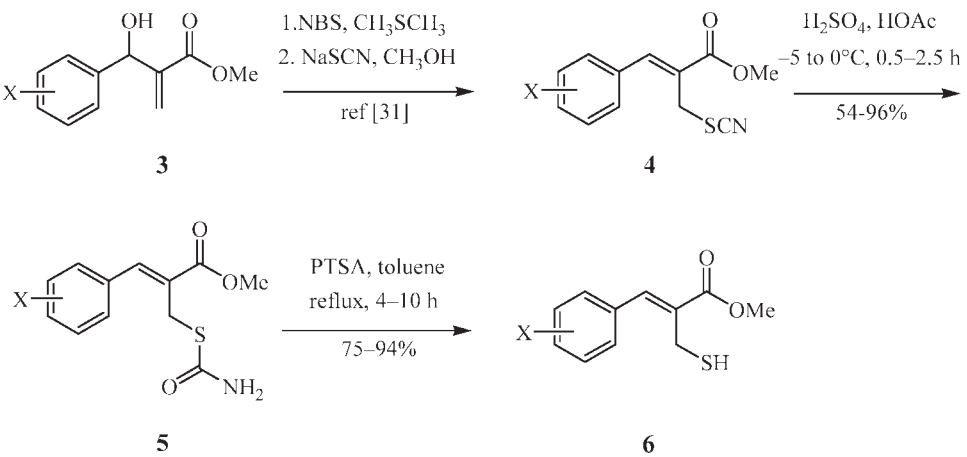


**Table 1**

Allyl thiocarbamates **5** and allyl thiols **6**.

| Entry | X | Reactant | Time (h) | Product | Yield (%) | Time[a] (h) | Product | Yield[a] (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | H | **4a** | 1 | **5a** | 75 | 7 (32) | **6a** | 94 (82) |
| 2 | 4-Cl | **4b** | 1 | **5b** | 84 | 4 (56) | **6b** | 89 (77) |
| 3 | 2-Cl | **4c** | 2.5 | **5c** | 85 | 10 | **6c** | 83 |
| 4 | 2-Br | **4d** | 2 | **5d** | 86 | 5 | **6d** | 77 |
| 5 | 2-F | **4e** | 1 | **5e** | 87 | 5 | **6e** | 78 |
| 6 | 4-$NO_2$ | **4f** | 1 | **5f** | 96 | 6 | **6f** | 85 |
| 7 | 2-$NO_2$ | **4g** | 0.5 | **5g** | 89 | 4 (26) | **6g** | 94 (68) |
| 8 | 4-Me | **4h** | 1 | **5h** | 54 | 7 | **6h** | 75 |

[a]Values in parentheses indicate when 0.1 equivalent of PTSA was used.

***Methyl (Z)-2-carbamoylthiomethyl-3-(2-chlorophenyl)propenoate (5c).*** Reaction time: 2.5 h; white solid; yield: 85%; mp: 102–103°C; ir (potassium bromide): 3419, 3326, 3308, 1698, 1662, 1607, 1438 $cm^{-1}$; $^1H$ NMR (deuteriochloroform): δ 3.87 (s, 3 H, $OCH_3$), 3.97 (s, 2 H, $CH_2$), 5.42 (s, 2 H, $NH_2$), 7.30–7.46 (m, 4 H, aromatic), 7.89 (s, 1 H, CH); $^{13}C$ NMR (deuteriochloroform): δ 27.7, 52.5, 126.8, 129.5, 129.6, 130.1, 130.2, 133.2, 134.1, 139.3, 167.0, 168.1. *Anal*. Calcd. for $C_{12}H_{12}ClNO_3S$: C, 50.44; H, 4.23; N, 4.90; S, 11.22. Found: C, 50.22; H, 4.12; N, 4.76; S, 11.03.

***Methyl (Z)-3-(2-bromophenyl)-2-(carbamoylthiomethyl)propenoate (5d).*** Reaction time: 2 h; white solid; yield: 86%; mp: 93–95°C; ir (potassium bromide): 3418, 3334, 1712, 1673, 1465, 1435 $cm^{-1}$; $^1H$ NMR (deuteriochloroform): δ 3.87 (s, 3 H, $OCH_3$), 3.94 (s, 2 H, $CH_2$), 5.47 (s, 2 H, $NH_2$), 7.20–7.39 (m, 3 H, aromatic), 7.62–7.64 (m, 1 H, aromatic), 7.82 (s, 1 H, CH); $^{13}C$ NMR (deuteriochloroform): δ 27.6, 52.5, 124.0, 127.4, 129.3, 130.2, 130.3, 132.8, 135.1, 141.4, 167.0, 168.0. *Anal*. Calcd. for $C_{12}H_{12}BrNO_3S$: C, 43.65; H, 3.66; N, 4.24; S, 9.71. Found: C, 43.42; H, 3.40; N, 4.38; S, 9.52.

***Methyl (Z)-2-(carbamoylthiomethyl)-3-(2-fluorophenyl)propenoate (5e).*** Reaction time: 1 h; white solid; yield: 87%; mp: 102–104°C; ir (potassium bromide): 3421, 3323, 3310, 3193, 1701, 1662, 1610, 1485, 1438 $cm^{-1}$; $^1H$ NMR (deuteriochloroform): δ 3.86 (s, 3 H, $OCH_3$), 4.04 (s, 2 H, $CH_2$), 5.42 (s, 2 H, $NH_2$), 7.09–7.49 (m, 4 H, aromatic), 7.85 (s, 1 H, CH); $^{13}C$ NMR (deuteriochloroform): δ 27.8, 52.4, 115.6 ($J$ = 22.0 Hz), 122.5 ($J$ = 13.4 Hz), 124.2, 129.6, 130.2, 131.0, 134.7, 160.4 ($J$ = 250 Hz), 167.0, 168.3. *Anal*. Calcd. for $C_{12}H_{12}FNO_3S$: C, 53.52; H, 4.49; N, 5.20; S, 11.91. Found: C, 53.70; H, 4.37; N, 5.02; S, 11.76.

***Methyl (Z)-2-(carbamoylthiomethyl)-3-(4-nitrophenyl)propenoate (5f).*** Reaction time: 1 h; white solid; yield: 96%; mp: 144–145°C; ir (potassium bromide): 3401, 3324, 1717, 1633, 1592, 1517, 1345 $cm^{-1}$; $^1H$ NMR (dimethyl sulfoxide-$d_6$): δ 3.78 (s, 3 H, $OCH_3$), 3.90 (s, 2 H, $CH_2$), 7.66 (s, 2 H, $NH_2$), 7.73 (s, 1H, CH), 7.76 (d, 2 H, $J$ = 8.8 Hz, aromatic), 8.27 (d, 2 H, $J$ = 8.8 Hz, aromatic); $^{13}C$ NMR (dimethyl sulfoxide-$d_6$): δ 26.2, 52.4, 123.6, 130.6, 131.6, 137.9, 141.1, 147.2, 165.7, 166.6. *Anal*. Calcd. for $C_{12}H_{12}N_2O_5S$: C, 48.64; H, 4.08; N, 9.45; S, 10.82. Found: C, 48.39; H, 4.27; N, 9.28; S, 10.63.

***Methyl (Z)-2-(carbamoylthiomethyl)-3-(2-nitrophenyl)propenoate (5g).*** Reaction time: 0.5 h; white solid; yield: 89%; mp: 113–114°C; ir (potassium bromide): 3436, 3335, 3175, 1712, 1680, 1606, 1522, 1437, 1344 $cm^{-1}$; $^1H$ NMR (deuteriochloroform): δ 3.79 (s, 2 H, $CH_2$), 3.87 (s, 3 H, $OCH_3$), 5.37 (s, 2 H, $NH_2$), 7.37–7.73 (m, 3 H, aromatic), 8.06 (s, 1 H, CH), 8.21–8.24 (m, 1 H, aromatic); $^{13}C$ NMR (deuteriochloroform): δ 27.3, 52.5, 124.9, 129.4, 129.5, 130.9, 131.2, 133.7, 139.2, 147.3, 166.7, 167.8. *Anal*. Calcd. for $C_{12}H_{12}N_2O_5S$: C, 48.64; H, 4.08; N, 9.45; S, 10.82. Found: C, 48.40; H, 3.88; N, 9.20; S, 10.59.

***Methyl (Z)-2-(carbamoylthiomethyl)-3-(4-methylphenyl)propenoate (5h).*** Reaction time: 1 h; white solid; yield: 54%; mp: 119–120°C; ir (potassium bromide): 3376, 3298, 1699, 1678, 1616, 1436 $cm^{-1}$; $^1H$ NMR (deuteriochloroform): δ 2.38 (s, 3 H, $CH_3$), 3.84 (s, 3 H, $OCH_3$), 4.13 (s, 2 H, $CH_2$), 5.49 (s, 2 H, $NH_2$), 7.23 (d, 2 H, $J$ = 7.9 Hz, aromatic), 7.37 (d, 2 H, $J$ = 7.9 Hz, aromatic), 7.80 (s, 1 H, CH); $^{13}C$ NMR (deuteriochloroform): δ 21.4, 28.0, 52.3, 126.0, 129.5, 129.7, 131.5, 139.6, 142.6, 167.8, 168.6. *Anal*. Calcd. for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70; N, 5.28; S, 12.09. Found: C, 58.61; H, 5.43; N, 5.03; S, 12.31.

**General procedure for the preparation of methyl (*Z*)-3-aryl-2-(mercaptomethyl)propenoates 6.** A stirred solution of thiocarbamate **5** (1 mmole) and PTSA (0.19 g, 1 mmole) in a mixture of toluene (9 mL) and dichloromethane (1 mL) was heated at reflux temperature for 4–10 h. After cooling to room temperature, the mixture was diluted with saturated aqueous sodium bicarbonate solution (5 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous magnesium sulfate and the solvent was evaporated *in vacuo*. The resulting mixture was chromatographed on silica gel eluting with hexane/ethyl acetate (15:1) to produce **6**.

The physical and spectral data of **6** prepared by this general method are as follows.

***Methyl (Z)-2-(mercaptomethyl)-3-phenylpropenoate (6a).*** Reaction time: 7 h; colorless oil; yield: 94%; ir (neat): 2571, 1712, 1628, 1493, 1447, 1434 $cm^{-1}$; $^1H$ NMR (deuteriochloroform): δ 2.06 (t, 1 H, $J$ = 7.9 Hz, SH), 3.60 (d, 2 H, $J$ = 7.9 Hz, $CH_2$), 3.87 (s, 3 H, $OCH_3$), 7.35–7.45 (m, 5 H, aromatic), 7.70 (s, 1 H, CH); $^{13}C$ NMR (deuteriochloroform): δ 21.2, 52.2, 128.7, 129.0, 129.3, 131.8, 134.8, 139.7, 167.4. *Anal*. Calcd. for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; S, 15.40. Found: C, 63.19; H, 5.75; S, 15.27.

***Methyl (Z)-3-(4-chlorophenyl)-2-(mercaptomethyl)propenoate (6b).*** Reaction time: 4 h; colorless oil; yield: 89%; ir (neat): 2573, 1712, 1630, 1591, 1489, 1435 $cm^{-1}$; $^1H$ NMR

(deuteriochloroform): δ 2.06 (t, 1 H, $J$ = 7.6 Hz, SH), 3.55 (d, 2 H, $J$ = 7.6 Hz, $CH_2$), 3.86 (s, 3 H, $OCH_3$), 7.36–7.41 (m, 4 H, aromatic), 7.63 (s, 1 H, CH); $^{13}$C NMR (deuteriochloroform): δ 21.1, 52.3, 129.0, 130.7, 132.3, 133.2, 135.0, 138.3, 167.1. *Anal*. Calcd. for $C_{11}H_{11}ClO_2S$: C, 54.43; H, 4.57; S, 13.21. Found: C, 54.22; H, 4.29; S, 12.90.

***Methyl (Z)-3-(2-chlorophenyl)-2-(mercaptomethyl)propenoate (6c).*** Reaction time: 10 h; colorless oil; yield: 83%; ir (neat): 2582, 1714, 1633, 1468, 1436 cm$^{-1}$; $^1$H NMR (deuteriochloroform): δ2.08 (t, 1 H, $J$ = 8.3 Hz, SH), 3.45 (d, 2 H, $J$ = 8.3 Hz, $CH_2$), 3.88 (s, 3 H, $OCH_3$), 7.31–7.48 (m, 4 H, aromatic), 7.76 (s, 1 H, CH); $^{13}$C NMR (deuteriochloroform): δ 21.3, 52.4, 126.9, 129.7, 129.9, 130.0, 133.5, 133.6, 134.1, 136.5, 166.8. *Anal*. Calcd. for $C_{11}H_{11}ClO_2S$: C, 54.43; H, 4.57; S, 13.21. Found: C, 54.31; H, 4.40; S, 13.03.

***Methyl (Z)-3-(2-bromophenyl)-2-(mercaptomethyl)propenoate (6d).*** Reaction time: 5 h; colorless oil; yield: 77%; ir (neat): 2574, 1714, 1633, 1464, 1434 cm$^{-1}$; $^1$H NMR (deuteriochloroform): δ 2.07 (t, 1 H, $J$ = 8.0 Hz, SH), 3.43 (d, 2 H, $J$ = 8.0 Hz, $CH_2$), 3.89 (s, 3 H, $OCH_3$), 7.23–7.65 (m, 4 H, aromatic), 7.70 (s, 1 H, CH); $^{13}$C NMR (deuteriochloroform): δ 21.2, 52.4, 124.0, 127.5, 130.0, 130.2, 132.9, 133.3, 135.4, 138.7, 166.8. *Anal*. Calcd. for $C_{11}H_{11}BrO_2S$: C, 46.01; H, 3.86; S, 11.17. Found: C, 45.88; H, 3.60; S, 11.31.

***Methyl (Z)-3-(2-fluorophenyl)-2-(mercaptomethyl)propenoate (6e).*** Reaction time: 5 h; white solid; yield: 78%; mp 32–34°C; ir (potassium bromide): 2557, 1708, 1632, 1608, 1482, 1461, 1434 cm$^{-1}$; $^1$H NMR (deuteriochloroform): δ 2.08 (t, 1 H, $J$ = 7.9 Hz, SH), 3.52 (d, 2 H, $J$ = 7.9 Hz, $CH_2$), 3.87 (s, 3 H, $OCH_3$), 7.08–7.51 (m, 4 H, aromatic), 7.72 (s, 1 H, CH); $^{13}$C NMR (deuteriochloroform): δ 21.4, 52.3, 115.8 ($J$ = 22.0 Hz), 122.8 ($J$ = 13.4 Hz), 130.1, 130.8, 130.9, 132.1, 133.8, 160.4 ($J$ = 250 Hz), 166.8. *Anal*. Calcd. for $C_{11}H_{11}FO_2S$: C, 58.39; H, 4.90; S, 14.17. Found: C, 58.52; H, 4.72; S, 14.02.

***Methyl (Z)-2-(mercaptomethyl)-3-(4-nitrophenyl)propenoate (6f).*** Reaction time: 6 h; yellowish solid; yield: 85%; mp 78–80°C; ir (potassium bromide): 2593, 1717, 1633, 1592, 1517, 1434, 1345 cm$^{-1}$; $^1$H NMR (deuteriochloroform): δ 2.12 (t, 1 H, $J$ = 7.7 Hz, SH), 3.53 (d, 2 H, $J$ = 7.7 Hz, $CH_2$), 3.90 (s, 3 H, $OCH_3$), 7.60 (d, 2 H, $J$ = 8.3 Hz, aromatic), 7.70 (s, 1 H, CH), 8.28 (d, 2 H, $J$ = 8.8 Hz, aromatic); $^{13}$C NMR (deuteriochloroform): δ 21.0, 52.6, 123.9, 130.0, 134.9, 136.8, 141.3, 147.6, 166.5. *Anal*. Calcd. for $C_{11}H_{11}NO_4S$: C, 52.16; H, 4.38; N, 5.53; S, 12.66. Found: C, 51.90; H, 4.02; N, 5.32; S, 12.37.

***Methyl (Z)-2-(mercaptomethyl)-3-(2-nitrophenyl)propenoate (6g).*** Reaction time: 4 h; yellowish solid; yield: 94%; mp 48–49°C; ir (potassium bromide): 2569, 1721, 1635, 1605, 1569, 1513, 1429, 1337 cm$^{-1}$; $^1$H NMR (deuteriochloroform): δ 2.08 (t, 1 H, $J$ = 8.2 Hz, SH), 3.33 (d, 2 H, $J$ = 8.2 Hz, $CH_2$), 3.89 (s, 3 H, $OCH_3$), 7.53–7.74 (m, 3 H, aromatic), 7.92 (s, 1 H, CH), 8.18–8.21 (m, 1 H, aromatic); $^{13}$C NMR (deuteriochloroform): δ 21.2, 52.4, 125.1, 129.6, 130.8, 131.0, 133.1, 133.8, 136.4, 147.4, 166.4. *Anal*. Calcd. for $C_{11}H_{11}NO_4S$: C, 52.16; H, 4.38; N, 5.53; S, 12.66. Found: C, 52.03; H, 4.11; N, 5.42; S, 12.82.

***Methyl (Z)-2-(mercaptomethyl)-3-(4-methylphenyl)-propenoate (6h).*** Reaction time: 7 h; colorless oil; yield: 75%; ir (neat): 2566, 1710, 1627, 1608, 1511, 1435 cm$^{-1}$; $^1$H NMR (deuteriochloroform): δ 2.05 (t, 1 H, $J$ = 7.6 Hz, SH), 2.38 (s, 3 H, $CH_3$), 3.60 (d, 2 H, $J$ = 7.6 Hz, $CH_2$), 3.85 (s, 3H, $OCH_3$), 7.23 (d, 2 H, $J$ = 7.9 Hz, aromatic), 7.35 (d, 2 H, $J$ = 7.9 Hz, aromatic), 7.67 (s, 1 H, CH); $^{13}$C NMR (deuteriochloroform): δ 21.3, 21.4, 52.2, 129.4, 129.5, 130.9, 131.9, 139.3, 139.8, 167.5. *Anal*. Calcd. for $C_{12}H_{14}O_2S$: C, 64.83; H, 6.35; S, 14.42. Found: C, 64.61; H, 6.22; S, 14.28.

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## REFERENCES AND NOTES

[1] Patai, S., Ed. The Chemistry of the Thiol Group; Wiley: New York, 1974, Part 1 and 2.

[2] Klein, L. L.; Yeung, M. C.; Kurath, P.; Mao, C. J.; Fernandes, B. P.; Lartery, P. A.; Pernet, A. G. J Med Chem 1989, 32, 151.

[3] Yeager, L. J.; Amirsakis, D. G.; Newmann, E.; Garrell, R. L. Tetrahedron Lett 1998, 39, 8409.

[4] Huang, D.; Liao, F.; Molesa, S.; Redinger, D.; Subramanian, V. J Electrochem Soc 2003, 150, G412.

[5] Han, C. C.; Hong, S. P.; Yang, K. F.; Bai, M. Y.; Huang, C. S.; Lu, C. H. Macromolecules 2001, 34, 587.

[6] For review, see: Walter, W.; Bode, K.-D. Angew Chem Int Ed Engl 1967, 6, 281.

[7] Erian, A. W.; Sherif, S. M. Tetrahedron 1999, 55, 7957.

[8] Wood, T. F.; Gardner, J. H. J Am Chem Soc 1941, 63, 2741.

[9] Bowden, K.; Chana, R. S. J Chem Soc Perkin Trans 2 1990, 2163.

[10] Beji, M.; Sbihi, H.; Baklouti, A.; Cambon, A. J Fluorine Chem 1999, 99, 17.

[11] Worthing, C. R., Ed. The Pesticide Manual, 9th ed.; British Crop Protection Council: London, 1991.

[12] Chen-Hsien, W. Synthesis 1981, 622.

[13] Goel, A.; Mazur, S. J.; Fattah, R. J.; Hartman, T. L.; Turpin, J. A.; Huang, M.; Rice, W. G.; Appella, E.; Inman, J. K. Bioorg Med Chem Lett 2002, 12, 767.

[14] (a) Mizuno, T.; Nishiguchi, I.; Okushi, T.; Hirashima, T. Tetrahedron Lett 1991, 32, 6867; (b) Chen, Y. S.; Schuphan, I.; Casida, J. E. J Agric Food Chem 1979, 27, 709.

[15] (a) Zheng, T.-C.; Burkart, M.; Richardson, E. D. Tetrahedron Lett 1999, 40, 603; (b) Gryko, T. D.; Clausen, C.; Roth, K. M.; Dontha, N.; Bocian, F. D.; Kuhr, W. G.; Lindsey, J. S. J Org Chem 2000, 65, 7345; (c) Li, W.; Lynch, V.; Thompson, H.; Fox, M. A. J Am Chem Soc 1997, 119, 7211; (d) Ohlsson, J.; Magnusson, G. Tetrahedron Lett 1999, 40, 2011; (e) Han, C.-C.; Balakumar, R. Tetrahedron Lett 2006, 47, 8255.

[16] Kim, S.; Ahn, K. H. J Org Chem 1984, 49, 1717.

[17] Houk, J.; Whitesides, G. M. J Am Chem Soc 1987, 109, 6825.

[18] Jaeger, A. D.; Su, D.; Zafar, A. J Am Chem Soc 2000, 122, 2749.

[19] Coates, R. M.; Ho, A. W. W. J Am Chem Soc 1969, 91, 7544.

[20] (a) Weiss, U. J Am Chem Soc 1947, 69, 2684; (b) Fang, Z.; Breslow, R. Bioorg Med Chem Lett 2005, 15, 5463.

[21] (a) Tilles, H. J Am Chem Soc 1959, 81, 714; (b) Reddy, T. I.; Bhawal, B. M.; Rajappa, S. Tetrahedron Lett 1992, 33, 2857.

[22] Wynne, J. H.; Jensen, S. D.; Snow, A. W. J Org Chem 2003, 68, 3733.

[23] Zil'berman, E. N.; Lazaris, A. Y. J Gen Chem USSR 1963, 33, 1012.

[24] Klásek, A.; Mrkvicka, V.; Pevec, A.; Košmrlj, J. J Org Chem 2004, 69, 5646.

[25] (a) Baylis, A. B.; Hillman, M. E. D. Ger. Pat.2,155,133 (1972); (b) Baylis, A. B.; Hillman, M. E. D. Chem Abstr 1972, 77, 34174q.

[26] (a) For reviews of the Baylis-Hillman reaction, see: Drewes, S. E.; Roos, G. H. P. Tetrahedron 1988, 44, 4653; (b) Basavaiah, D.; Rao, P. D.; Hyma, R. S. Tetrahedron 1996, 52, 8001; (c) Ciganek, E. Org React 1997, 51, 201; (d) Langer, P. Angew Chem Int Ed 2000, 39, 3049; (e) Basavaiah, D.; Rao, A. J.; Santyanarayana, T. Chem Rev 2003, 103, 811; (f) Kataoka, T.; Kinoshita, H. Eur J Org Chem 2005, 45; (g) Singh, V.; Batra, S. Tetrahedron 2008, 64, 4511.

[27] (a) For our recent examples, see: Song, Y. S.; Lee, C. H.; Lee, K.-J. J Heterocycl Chem 2003, 40, 939; (b) Lee, C. H.; Song, Y. S.; Cho, H. I.; Yang, J. W.; Lee, K.-J. J Heterocycl Chem 2003, 40, 1103; (c) Ko, S. H.; Lee, K.-J. J Heterocycl Chem 2004, 41, 613; (d) Lee, C. H.; Lee, K.-J. Synthesis 2004, 1941; (e) Hong, W. P.; Lee, K.-J. Synthesis 2005, 33; (f) Hong, W. P.; Lee, K.-J. Synthesis 2006, 963; (g) Yi, H.-W.; Park, H. W.; Song, Y. S.; Lee, K.-J. Synthesis 2006, 1953; (h) Lim, H. N.; Ji, S.-H; Lee, K.-J. Synthesis 2007, 2454; (i) Song, Y. S.; Lee, K.-J. Synthesis 2007, 3037; (j) Lim, H. N.; Song, Y. S.; Lee, K.-J. Synthesis 2007, 3376; (k) Jeon, K. J.; Lee, K.-J. J Heterocycl Chem 2008, 45, 615.

[28] (a) Liu, Y.; Xu, X.; Zheng, H.; Xu, D.; Xu, Z.; Zhang, Y. Synlett 2006, 5671; (b) Srihari, P.; Singh, A.P.; Jain, R.; Yadav, J. S. Synthesis 2006, 2772; (c) Das, B.; Chowdhury, N.; Damodar, K.; Banerjee J. Chem Pharm Bull 2007, 55, 1274.

[29] Cha, M. J.; Song, Y. S.; Lee, K.-J. Bull Korean Chem 2006, 27, 1900.

[30] Cha, M. J.; Song, Y. S.; Han, E.-G.; Lee, K.-J. J Heterocycl Chem 2008, 45, 235.

[31] Sá, M. M.; Fernandes, L.; Ferreira, M.; Bortoluzzi, A. J. Tetrahedron Lett 2008, 49, 1228.

[32] Das, B.; Venkateswarlu, K.; Krishnaiah, M.; Holla, H.; Majhi, A. Helv Chim Acta 2006, 89, 1417.