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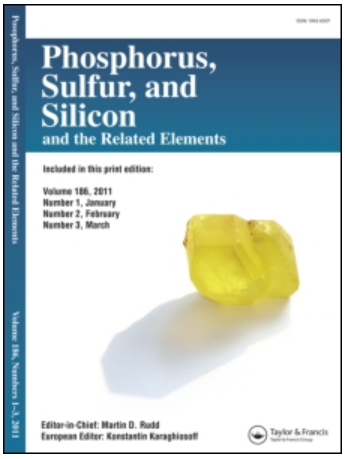

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Michael Addition Reaction of Thioacetic Acid (AcSH) to Conjugated Alkenes Under Solvent- and Catalyst-Free Conditions

Sara Sobhani[a]; Soodabeh Rezazadeh[a]
[a] Department of Chemistry, College of Sciences, Birjand University, Birjand, Iran

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MICHAEL ADDITION REACTION OF THIOACETIC ACID (AcSH) TO CONJUGATED ALKENES UNDER SOLVENT- AND CATALYST-FREE CONDITIONS

Sara Sobhani and Soodabeh Rezazadeh
Department of Chemistry, College of Sciences, Birjand University, Birjand, Iran

A new and convenient procedure has been developed for the Michael addition reaction of thioacetic acid (AcSH) to a variety of conjugated alkenes under solvent- and catalyst-free conditions. These reactions proceeded in 5–60 min and produced the desired products in good to high yields.

Keywords Catalyst-free; conjugated alkenes; Michael addition; solvent-free; thioacetic acid

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INTRODUCTION

The thia-Michael addition is one of the most versatile and practical reactions for C—S bond formation in organic synthesis.[1] The conversion of α,β-unsaturated carbonyl compounds to the corresponding β-sulfido carbonyl derivatives provides a strategy for the chemoselective protection of olefinic double bonds.[2] In addition, these compounds are starting materials for the generation of β-acylvinyl cations[3] and homoenolate anion equivalents.[4] For these and other reasons, the thia-Michael addition is an important reaction in organic synthesis and plays a critical role in biosynthesis and the synthesis of bioactive compounds.[5] To date, a great deal of effort has been directed toward the use of strong nucleophilic thiols such as alkyl and aryl thiols as Michael donors in the Michael addition reaction.[6,7] Generally, harsh reaction conditions are required for the conversion of the newly formed C—S bond to more a synthetically versatile SH group.[8] On the other hand, the use of thioacids (RCOSH) as nucleophiles for the Michael addition reaction is more attractive, since the resulting thioesters can be readily transformed into a SH group under various mild reaction conditions.[8] A literature survey indicates that in contrast to the existing methods for the Michael addition of alkyl and aryl thiols to enones, few methods are known for the use of thioacids as Michael donors.[9–14] However, the reported procedures suffer from at least one of the following drawbacks such as low yields of the products,[9] use of toxic solvents,[9,10] and long reaction times.[9–11] Piperidine[11] and diethylamine[12] have been reported as the common basic catalysts for conjugate addition of thioacetic acid (AcSH) to the enones. These methods suffer from usually low yields and long reaction times (18–24 h). $SnCl_4$ is a Lewis acid catalyst that was used to achieve this kind of Michael addition reaction. In this method, the product was isolated in a very low yield (8%) after a long reaction time (68 h).[10] Therefore, it is necessary to develop an efficient and convenient method for the thia-Michael addition reaction of AcSH to conjugated alkenes.

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Address correspondence to Sara Sobhani, Department of Chemistry, College of Sciences, Birjand University, Birjand 414, Iran. E-mail: sobhanisara@yahoo.com

Table I Optimization of the Michael addition reaction of AcSH to 4-phenylbut-3-en-2-one

Entry	Conjugated alkene:AcSH	Temperature (°C)	Solvent	Time (h)	Yield[a] (%)
1	1:1	rt	—	24	40
2	1:1	50	—	24	50
3	1:1	80	—	24	50
4	1:1	rt	Et_2O	24	50
5	1:1	rt	$CHCl_3$	24	5
6	1:1	rt	CH_2Cl_2	24	20
7	1:1	rt	Toluene	24	10
8	1:2	rt	—	1	85

[a]Isolated yield.

From both economic and environmental viewpoints, organic reactions under solvent- and catalyst-free conditions have gained popularity in recent years. This is because solvent- and catalyst-free reactions are greener and eliminate waste. Solvent-free reactions are generally fast and give higher selectivity and yields, which may offer advantages over those occurring in organic solvents.[15]

As a part of our research aimed at developing green chemistry by using water as the reaction medium or by performing organic transformations under solvent-free conditions,[16] in this article we describe a highly efficient, simple, and eco-friendly method for the Michael addition reaction of AcSH to different conjugated alkenes without the use of catalyst or solvent.

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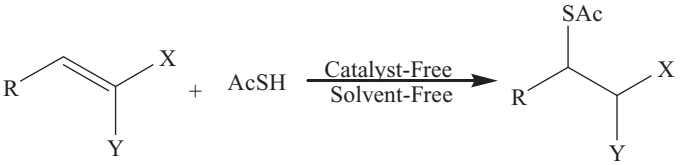
RESULTS AND DISSCUSION

In order to find the best reaction conditions, the Michael addition reaction of AcSH to 4-phenylbut-3-en-2-one was studied as a model reaction under solvent-free conditions at the temperature range of 25°C to 80°C. It was found that the temperature change did not show a strong effect on the reaction yield, and the desired product was formed in only 40–50% yields after 24 h (Table I, entries 1–3). Then, a similar reaction was studied in different solvents at room temperature, and again the product was obtained in low yields (Table I, entries 4–7). The best result was found when the reaction was performed in the presence of an excess amount of AcSH under solvent-free conditions at room temperature (Table I, entry 8).

With optimal conditions in hand, we examined the generality of this procedure by the reaction of different conjugated alkenes with AcSH (Scheme 1, Table II).

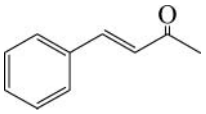
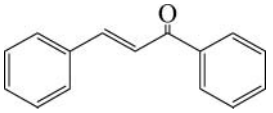
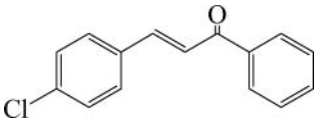
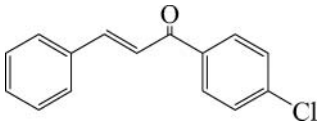
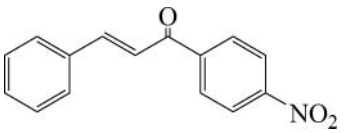
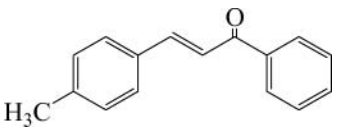
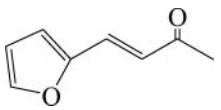
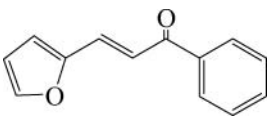
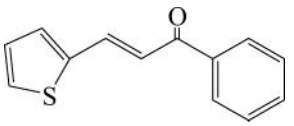
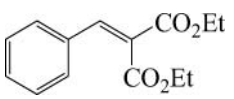


R=H, aryl, heteroaryl
X=C(O)R' [R'=alkyl, aryl, alkoxy], NO_2
Y=H, Me, CO_2Et

1-13

Scheme 1

Table II Michael addition reaction of AcSH[a] to conjugated alkenes under solvent- and catalyst-free conditions

Entry[b]	Conjugated alkenes	Product[ref]	Time (min)	Yield[c] (%)
1		**1**[13]	60	85
2		**2**[13]	5	93
3		**3**[13]	5	98
4		**4**[13]	5	90
5		**5**	5	85
6		**6**	5	98
7		**7**	5	95
8		**8**	15	97
9[d]		**9**	5	97
10		**10**	30	85

(Continued on next page)

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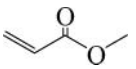
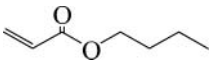
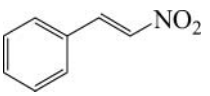
Table II Michael addition reaction of AcSH[a] to conjugated alkenes under solvent- and catalyst-free conditions *(Continued)*

Entry[b]	Conjugated alkenes	Product[ref]	Time (min)	Yield[c] (%)
11		**11**	15	75
12		**12**	5	76
13		**13**[14]	5	98

[a]Conditions: AcSH (2 equiv.).
[b]Conditions: room temperature (except for entry 10).
[c]Isolated yields.
[d]Conditions: 50°C.

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As it is indicated in Table II, chalcone derivatives carrying either an electron-donating or an electron-withdrawing substitute reacted in short reaction times to give the desired products in high yields (entries 2–6). Heterocyclic systems (e.g., thiophene and furan, Table II, entries 7–9) were also effective substrates to successfully execute Michael addition reactions under the similar reaction conditions. In all of these reactions, no byproducts resulting from the undesired 1,2-addition and/or bis-addition reaction were observed. In addition to α,β-unsaturated ketones, some other conjugated alkenes were also screened to carry out the conjugate addition by AcSH under solvent-free conditions. For α,β-unsaturated malonate, esters, and nitro compound, the reaction worked well and the expected products (**10–13**) were obtained in 75–98% yields (Table II, entries 10–13). The Michael addition reaction of AcSH to cinnamaldehyde produced the desired product with low yield (40%) due to the formation of a byproduct resulting from 1,2-addition reaction of AcSH to carbonyl group.

In order to show the advantages of the present work in comparison with other reported protocols, we compared the reaction conditions of this method with those reported previously (Table III).

As shown in Table III, the reported procedures for the catalyst-free Michael addition reaction of AcSH to conjugated alkenes required long reaction times to produce the desired products in low to moderate yields (entries 2–4). The reaction resulted in the Michael addition product in good to high yields in the presence of chiral catalysts, but in low to moderate ee, probably due to the catalyst-free Michael addition reaction (background reaction) (Table III, entries 5 and 6).

In conclusion, we have introduced an experimentally simple and convenient process for the Michael addition reaction of AcSH to a variety of Michael acceptors under solvent- and catalyst-free conditions. Short reaction times, good to high yields, no side product formation, and simple extractive work-up make this method an attractive and a useful contribution to the present methodologies.

EXPRIMENTAL

Chemicals were purchased from Merck and Fluka Chemical Companies. IR spectra were run on a Perkin Elmer 780 instrument. NMR spectra were recorded on a Bruker

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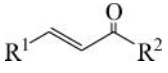
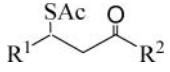
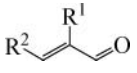
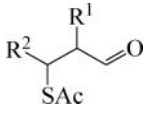
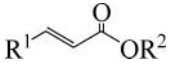
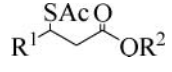
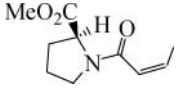
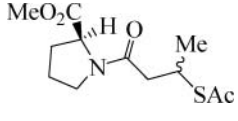
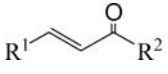
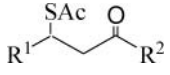
Table III Comparison of reaction conditions of the present method with those reported in the literature

Entry	Conjugated alkenes	Reagent or catalyst	Conditions	Product	Time	Yield (%)	Ref.
1		No catalyst	Solvent-free, rt, AcSH (2 equiv.)		5–60 min	75–98	—
2		No catalyst	Solvent-free, rt, AcSH (1.4 equiv.)		16 h	67–77	11d
3		No catalyst	CH_2Cl_2 and solvent-free, rt, AcSH (20 equiv.)		15–40 h	3–73	9
4		No catalyst or $SnCl_4$	CH_2Cl_2, −50 to 0°C, AcSH (3 equiv.)		68 h	8–86[a]	10
5		Chiral bifunctional amine thiourea	Rt, Et_2O, AcSH (2 equiv.)		3–24 h	75–100[b]	13

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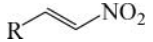
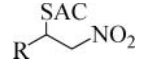
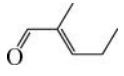
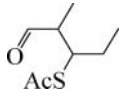
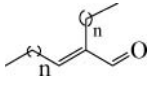
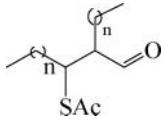
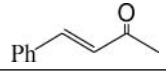
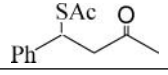
6		Quinidine	Et_2O, −15°C, AcSH (2 equiv.)		0.5–1.5 h	91–98[c]	14
7		Piperidine	Solvent-free, rt, AcSH (1.5 equiv.)		18 h	82	11a
8		Piperidine	Solvent-free, rt, AcSH (1.5 equiv.)		18 h	62–98	11b
9		Et_2NH	−80°C		24 h	35	12

[a]d.r. = 50–73%.
[b]ee = 0–65%.
[c]ee = 20–70%.

Avance DPX-250. Mass spectra were recorded on a Shimadzu GCMS-QP5050A. The purity of the products and the progress of the reactions were accomplished by TLC on silica-gel polygram SILG/UV_{254} plates. Elemental analysis for C and H were obtained using a Heraeus CHN-O-Rapid analyzer.

General Procedure for the Michael Addition Reaction of AcSH to Conjugated Alkenes

A mixture of conjugated alkene (1 mmol) and AcSH (2 mmol) was stirred for an appropriate time at room temperature or at 50°C (Table I). Then ethyl acetate (2 mL) was added to the reaction mixture, and the pure product was isolated from this mixture by plate chromatography eluted with *n*-hexane:EtOAc (10–5:1).

Spectral Data for Selected Products

Thioacetic acid S-[1-(4-nitro-phenyl)-3-oxo-3-phenyl-propyl) ester (5). ^{1}H NMR ($CDCl_3$, TMS): δ 2.33 (s, 3 H), 3.62–3.81 (m, 2 H), 5.20 (t, 1 H, $J = 6.5$ Hz), 7.23–7.32 (m, 5 H), 8.08 (d, 2 H, $J = 8.8$ Hz), 8.30 (d, 2 H, $J = 8.8$ Hz) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 30.4, 43.5, 45.3, 123.9, 127.7, 128.8, 129.2, 139.6, 140.7, 146.8, 150.4, 194.6, 195.1 ppm; IR (neat): ν 1685, 1662 (CO) cm^{-1}; MS (70 eV), m/e: 330 (M^++1), 150 (100%). Anal. Calcd. for $C_{17}H_{15}NO_4S$: C, 61.99; H, 4.59. Found: C, 61.98; H, 4.57%.

Thioacetic acid S-[1-(4-methyl-phenyl)-3-oxo-3-phenyl-propyl) ester (6). ^{1}H NMR ($CDCl_3$, TMS): δ 2.31 (s, 6 H), 3.64–3.71 (m, 2 H), 5.28 (t, 1 H, $J = 7.8$ Hz), 7.12 (d, 2 H, $J = 8.0$ Hz), 7.29 (d, 2 H, $J = 7.8$ Hz), 7.45 (t, 2 H, $J = 7.5$ Hz), 7.56 (t, 1 H, $J = 6.8$ Hz), 7.96 (d. 2 H, $J = 8.3$ Hz) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 21.2, 30.4, 43.3, 44.6, 127.6, 128.2, 128.6, 129.4, 133.3, 136.5, 137.2, 137.5, 194.7, 196.5 ppm; IR (neat): ν 1679, 1671 (CO) cm^{-1}; MS (70 eV), m/e: 298 (M^+), 105 (100%). Anal. Calcd for $C_{18}H_{18}O_2S$: C, 72.54; H, 6.08. Found: C: 72.52; H, 6.05%.

Thioacetic acid S-[1-(furan-2-yl)-3-oxo-butyl) ester (7). ^{1}H NMR ($CDCl_3$, TMS): δ 2.11 (s, 3 H), 2.27 (s, 3 H), 3.00 (dd, 1 H, $J = 17.3$ Hz, $J = 6.3$ Hz), 3.15 (dd, 1 H, J = 17.0 Hz, J = 8.3 Hz), 5.14 (t, 1 H, $J = 7.8$ Hz), 6.17 (s, 1 H), 6.23 (s, 1 H), 7.24 (s, 1 H) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 29.9, 30.3, 36.1, 46.6, 107.1, 110.5, 142.0, 152.4, 193.9, 204.4 ppm; IR (neat): ν 1677, 1681 (CO) $cm^{-1;}$ MS (70 eV), m/e: 212 (M^+), 137 (100%). Anal. Calcd for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70. Found: C, 56.58; H, 5.69%.

Thioacetic acid S-[1-(furan-2-yl)-3-oxo-3-phenyl-propyl] ester (8). ^{1}H NMR ($CDCl_3$, TMS): δ 2.32 (s, 3 H), 3.62 (dd, 1 H, $J = 17.3$ Hz, $J = 6.0$ Hz), 3.73 (dd, 1 H, $J = 17.3$ Hz, $J = 8.0$ Hz), 5.39 (t, 1 H, $J = 7.8$ Hz), 6.25 (s, 2 H), 7.29 (s, 1 H), 7.45 (t, 2 H, $J = 7.3$ Hz), 7.56 (t, 1 H, $J = 7$ Hz), 7.95 (d, 2 H, $J = 7.3$ Hz) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 30.4, 36.6, 42.0, 107.2, 110.6, 128.1, 128.7, 133.4, 136.3, 142.0, 152.6, 194.1, 195.9 ppm; IR (neat): ν 1677 (CO) cm^{-1}; MS (70 eV), m/e: 274 (M^+), 105 (100%). Anal. Calcd for $C_{15}H_{14}O_3S$: C, 56.67; H, 5.14. Found: C, 56.66; H, 5.12%.

Thioacetic acid S-[1-(thiophen-2-yl)-3-oxo-3-phenyl-propyl] ester (9). ^{1}H NMR ($CDCl_3$, TMS): δ 2.32 (s, 3 H), 3.73 (d, 2 H, $J = 6.5$ Hz), 5.58 (t, 1 H, $J = 7$ Hz) 6.88 (t, 1 H, $J = 3.8$ Hz), 7.03 (d, 1 H, $J = 3.3$ Hz), 7.15 (d, 1 H, $J = 5.3$ Hz), 7.46 (t, 2 H, $J = 7.3$ Hz), 7.57 (t, 1 H, $J = 7.3$ Hz), 7.95 (d, 2 H, $J = 7.5$ Hz) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 30.3, 38.6, 45.3, 124.8, 125.7, 126.7, 128.1, 128.7, 133.4, 136.4, 144.0, 194.3,

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195.9 ppm; IR (neat): ν 1671 (CO) cm^{-1}; MS (70 eV), m/e: 290 (M^+), 105 (100%). Anal. Calcd for $C_{15}H_{14}O_2S_2$: C, 62.04; H, 4.86. Found: C, 62.02; H, 4.84%.

Diethyl 2-(acetylthio(phenyl)methyl)malonate (10). ^1H NMR ($CDCl_3$, TMS): δ 1.02 (t, 3 H, $J = 7.0$ Hz), 1.22 (t, 3 H, $J = 7.0$ Hz), 2.24 (s, 3 H), 3.94–4.02 (m, 3 H), 4.17 (q, 2 H, $J = 7.0$ Hz), 5.31 (d, 1 H, $J = 10$ Hz), 7.18–7.35 (m, 5 H) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 13.7, 13.9, 30.3, 45.9, 57.1, 61.7, 61.8, 127.8, 128.1, 128.5, 128.8, 139.3, 166.3, 166.8, 192.7 ppm; IR (neat): ν 1722, 1718, 1686 (CO) cm^{-1}; MS (70 eV), m/e: 325 (M^++1), 249 (100%). Anal. Calcd for $C_{16}H_{20}O_5S$: C, 59.24; H, 6.21. Found: C, 59.21; H, 6.19%.

Methyl 3-(acetylthio)propanoate (11). ^1H NMR ($CDCl_3$, TMS): δ 2.31 (s, 3 H), 2.61 (t, 2 H, $J = 7.0$ Hz), 3.08 (t, 2 H, $J = 7.0$ Hz), 3.67 (s, 3 H) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 24.2, 30.5, 34.1, 51.8, 172.1, 195.5 ppm; IR (neat): ν 1688 (CO) cm^{-1}; MS (70 eV), m/e: 162 (M^+), 43 (100%). Anal. Calcd for $C_6H_{10}O_3S$: C, 44.43; H, 6.21. Found: C, 44.42; H, 6.18%.

Butyl 3-(acetylthio)propanoate (12). ^1H NMR ($CDCl_3$, TMS): δ 0.90 (t, 3 H, $J = 7.3$ Hz), 1.28–1.42 (m, 2 H), 1.52–1.67 (m, 2 H), 2.31 (s, 3 H), 2.59 (t, 2 H, $J = 7.0$ Hz), 3.08 (t, 2 H, $J = 7.0$ Hz), 4.06 (t, 2 H, $J = 6.8$ Hz) ppm; ^{13}C NMR ($CDCl_3$, TMS): δ 13.7, 19.0, 24.2, 30.5, 34.3, 64.6, 171.7, 195.6 ppm; IR (neat): ν 1678, 1685 (CO) cm^{-1}; MS (70 eV), m/e: 204 (M^+), 43 (100%). Anal. Calcd for $C_9H_{16}O_3S$: C, 52.91; H, 7.89. Found: C, 52.87; H, 7.85%.

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