# Microwave Assisted *N*-Alkenyl Condensation between Pyrrolidine-2-thione and Various Aldehydes

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A series of *N*-alkenyl pyrrolidine-2-thiones were synthesized by the reaction between pyrrolidine-2-thione and various aldehydes such as *n*-propanal, isopropanal, *n*-butanal, *n*-hexanal, *n*-octanal and phenylacetaldehyde in 32-86% yields using microwave irradiation technique. Only one structural *E* isomers were predominantly formed within 15 minutes in chlorobenezene/*p*-toluenesulfonic acid monohydrate.

**Key Words :** Microwave irradiation, Pyrrolidine-2-thione, *N*-Alkenyl pyrrolidine-2-thiones, *N*-Alkenyl condensation

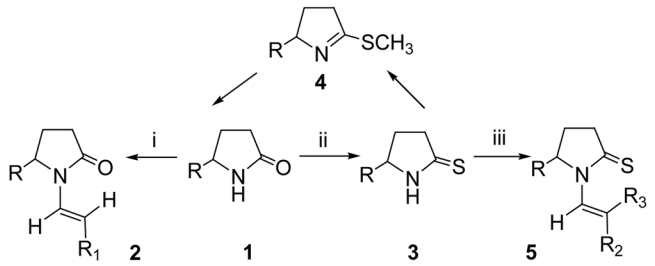
## Introduction

*N*-Vinyl analogues are widely used as very important intermediates in polymerizations,[1] alkaloid syntheses,[2] protecting procedure[3], Diels-Alder reactions[4], regioselective Heck couplings[5] and pyrimidine syntheses.[6] Whereas numerous reaction methods for the preparation of *N*-vinyl analogues have been previously reported using dehydration,[7] dehydroalkoxylation,[8] copper[9] and palladium[10] catalyzed vinylation, coupling with 2-halo vinyliodides,[11] and decomposition of acyloxy ethyl derivatives,[12] introducing vinyl moieties at the nitrogen atom in lactams have not been generally studied.

Recently microwave irradiation techniques for a variety of organic reactions are of great interest. Compared to the well-known conventional heating methods, high efficiency heating using microwave irradiation has been shown to dramatically accelerate reaction rates and reduce the reaction time with high yields.[13] We have demonstrated that a variety of reactions such as Knoevenagel condensations,[14] Michael addition,[15] nitration or *O*-alkylation in the aromatic rings,[16] and Friedlander type quinoline synthesis[17] can be facilitated by the microwave irradiation technique in the presence or absence of solvents. Although many microwave enhanced organic reactions have been explored, direct *N*-alkenylation reactions and their applications for the protection of NH atom in the lactam rings were poorly studied. More recently, in the course of investigation aimed at the synthesis of $\gamma$-vinyl amino butyric acid,[18] our prior extensive study has shown that lactam N-H **1** can be successfully condensed with several different types of aldehydes to give *N*-alkenyl analogues **2** under a conventional heating method using the Dean-Stark apparatus[19] or under microwave irradiation[15] conditions within a short period of time. The pyrrolidine-2-thione compounds, **3** are also of synthetic value. For example, **3** can be easily transformed to the *S*-methyl (R = $CH_3$) or *S*-benzyl (R = $CH_2Ph$) compounds **4**, by refluxing with methyl iodide in tetrahydrofuran and are also readily converted to the parent pyrrolidine-2-one, **1** in the presence of aqueous hydroiodide. Even though some alkaloids and total synthesis using *N*-alkyl thiolactams have been reported,[20] syntheses and applications of *N*-alkenyl pyrrolidine-2-thione, **5** using microwave irradiation technique have been rarely investigated so far. In here, we wish to represent the first successful application of microwave irradiation for the reaction between pyrrolidine-2-thione, **3** and a variety of aldehydes.

## Results and Discussion

Pyrrolidine-2-thione, **3** was synthesized by refluxing of pyrrolidine-2-one, **1** and Lawesson's reagent in toluene as previously described in the literature.[21] We initially examined eco-friendly *N*-alkenylation of **3** in the absence of solvent using a conventional microwave oven. However, these reactions were not successful and the yield from GC-MS analysis showed as low as 0-5% in $K_{10}$ or bentonite in $Al_2O_3$ (Table 1, entries 1-5). Using solvent for the condensation, the yields were significantly improved in our experimental conditions. It was found that chlorobenzene was the best




(i) R–CHO, toluene, *p*-TsOH, microwave irradiation
R=H or $CO_2Et$, $R_1$= $CH_3$, $CH_2CH_3$
(ii) Lawesson's reagent, toluene
(iii) R–CHO, chlorobenzene, *p*-TsOH, microwave irradiation
R=H
$R_2$= $CH_3$, $CH_2CH_3$, $CH_2(CH_2)_2CH$, $CH_2(CH_2)_4CH_3$, Ph
$R_3$= H, $CH_3$

**Scheme 1**

**Table 1**. Microwave assisted *N*-alkenyl condensation of lactam-2-thione, **3** with aldehydes using different solid supports and solvents (irradiation time: 15 min)

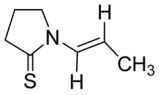
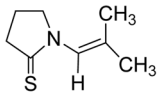
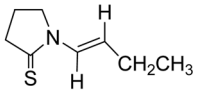
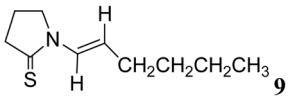
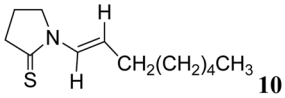
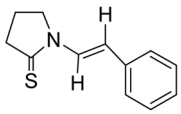
| Entry | aldehyde [a] | catalyst /solid support | solvent | yield (%) [b] |
|---|---|---|---|---|
| 1 | hexanal | none/$Al_2O_3$ | none | 0 |
| 2 | hexanal | $K_{10}/Al_2O_3$ | none | 0 |
| 3 | hexanal | none/bentonite | none | 5 |
| 4 | octanal | $K_{10}/Al_2O_3$ | none | 3 |
| 5 | octanal | *p*-TsOH/none | none | 0 |
| 6 | octanal | *p*-TsOH/none | *m*-xylene | 47[c] |
| 7 | octanal | *p*-TsOH/none | chlorobenzene | 59[c] |

[a]Mole ratio of **3**: aldehydes = 1:1.5. [b]Yields based on quantitative GC-MS analysis. [c]Isolated yields based on starting pyrrolidin-2-thiones after purification.

choice as an energy-transfer medium since its boiling point (131-133 °C) is about 30 °C higher than water, which is to be eliminated in the process. When the reaction was performed in *m*-xylene and chlorobenzene, we obtained 47 and 59% yields (Table 1, entries 6 and 7) respectively which were remarkably higher than using other solvents such as benzene or toluene. To avoid a solvent pressure in the reaction vessel, a large vial with a loose cap or an erlenmeyer flask with a funnel as a loose top was used. The microwave irradiation was carried with 3 minutes intervals and addition of chlorobenzene (1-3 mL) was necessary due to slight solvent evaporation.

This reaction condition is directly applicable to the synthesis for a variety of *N*-alkenyl thiolactams. As shown in Table 2, a series of *N*-alkenyl pyrrolidine-2-thiones were successfully synthesized by the microwave assisted condensation of pyrrolidin-2-thione with *n*-propanal, isopropanal, *n*-butanal, *n*-hexanal, *n*-octanal and phenylacetaldehyde. The results of our studies suggest a strong dependence of boiling point of aldehydes. As the boiling point of aldehydes increased, greater yields were obtained. This is probably due to the lower evaporating loss of higher boiling aldehydes in

**Table 2**. *N*-alkenyl condensation of lactam-2-thione, **3** with various aldehydes under conventional heating *versus* microwave assisted irradiation (MWI)

| Entry | Aldehyde [a] | Product [b] | Rf (100% $CH_2Cl_2$) | Yield (%) [c] | |
|---|---|---|---|---|---|
| | | | | $\Delta$[d] | MWI [e] |
| 1 | $CH_3CH_2CHO$ |  **6** | 0.60 | 6 | 32 |
| 2 | $(CH_3)_2CHCHO$ |  **7** | 0.52 [f] | – | 36 |
| 3 | $CH_3CH_2CH_2CHO$ |  **8** | 0.57 | 5 | 51 |
| 4 | $CH_3(CH_2)_3CH_2CHO$ |  **9** | 0.77 | 5 | 41 |
| 5 | $CH_3(CH_2)_5CH_2CHO$ |  **10** | 0.37 [g] | – | 59 |
| 6 | $PhCH_2CHO$ |  **11** | 0.68 [h] | – | 86 |

[a]Mole ratio of pyrrolidin-2-thiones:aldehyde = 1:1.5, solvent:chlorobenzene). [b]Catalyst: *p*-TsOH, reaction time: 15 min. [c]Isolated yields based on starting pyrrolidin-2-thiones. [d]Oil bath temperature = 135 °C. [e]Conventional Microwave oven. [f]10% Hexane in $CH_2Cl_2$. [g]50% Hexane in $CH_2Cl_2$. [h]20% Hexane in $CH_2Cl_2$.

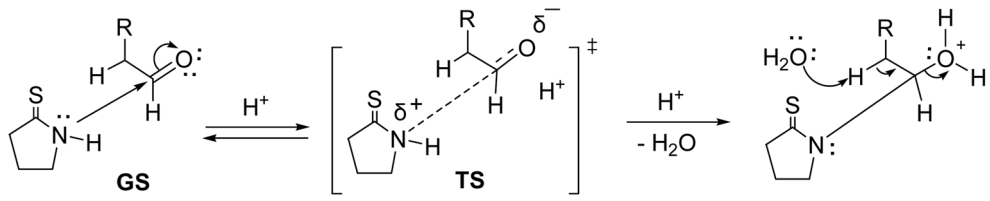



**Figure 1**. Proposed mechanism for the ground state (**GS**) *versus* dipole-dipole electrostatic transition state (**TS**) between pyrrolidin-2-thione and aldehyde.

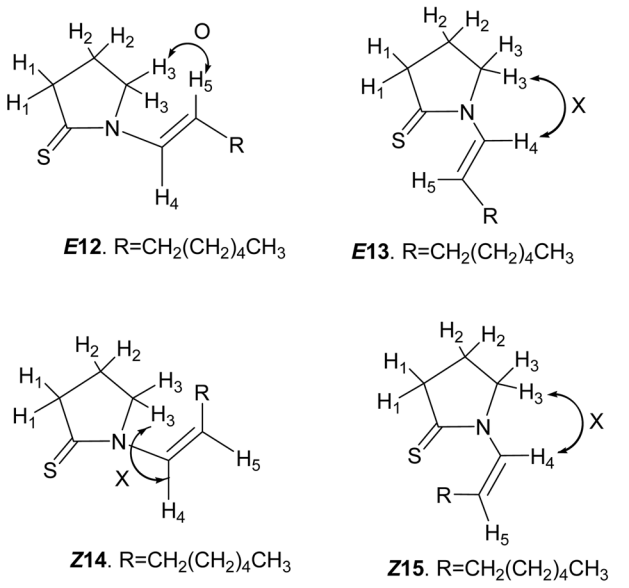



**Figure 2**. *E (**E12** and **E13**)/Z* (***Z*14** and ***Z*15**) alkene isomer structures and observed NOE interactions between H-3 and H-5 in ***E12***.

the reaction media. In the case of phenylacetaldehyde (bp = 195 °C), we obtained the highest yield as a 91% (entry 6). All thiolactam alkenyl products (**6**, **7**, **8**, **9** and **10**) were isolated as an oil form except the phenylacetaldehyde derivative (**11**, mp = 118-120 °C).

The experimental results using microwave irradiation (MWI) and conventional heating were compared to see non-thermal MW effects. The same reaction conditions like vessel temperature, reaction time and mole ratio used under MW were performed in the conventional heating experiments using a preheated oil bath (Table 2, entries 1, 3, and 4). In all cases, conventional heating gave considerably low yields which clearly proves the efficacy of the specific and non-thermal MW effects. It has been emphasized that specific MW effects were generally observed for polar mechanism from the ground state (GS) towards the transition state (TS) when the polarity increased.[13a,23] As shown in the proposed mechanism (Figure 1), the formation of *N*-alkenyl product (**5**) was accelerated by microwave irradiation due to the electric field induced dipole-dipole intermediate in the rate-determining step. The intermolecular nucleophilic addition of lactam nitrogen to the aldehyde carbonyl carbon in the **GS** involves the formation of an electrostatic polarized **TS** which is stabilized under microwave conditions. Further elimination of 1 equivalent of water gave *N*-alkenylated products (**5**) in an mild acidic medium.

*E/Z* alkene isomers can be often determined on the basis of large coupling constants (*J*) as ascertained by $^1$H NMR. Large coupling constants of *E* alkenyl hydrogens of **6** at $\delta$ 7.54 (*J* = 13.05 Hz), **8** at $\delta$7.49 (*J* = 14.5 Hz), **9** at $\delta$7.48 (*J* = 14.46 Hz), **10** at $\delta$7.48 (*J* = 14.58 Hz) and **11** at $\delta$8.27 (*J* = 15.03 Hz) ppm were observed respectively in the $^1$H NMR. We have also performed two-dimensional NOESY experiments to evaluate the neighborhood proton influence. Figure 2 shows four possible *E* or *Z* isomer structures (***E*12**, ***E*13**, ***Z*14** and ***Z*15**) of octenyl thiolactam (**10**). Interacting NOE cross peaks between H-3 on the thio-lactam ring and the closest proton H-5 of the alkenyl moiety were observed as shown in ***E*12**. No cross peaks corresponding to the proton interactions between H-3 and H-4 were observed (***E*13**, ***Z*14** and ***Z*15**). We thus determined that *E* isomers were predominantly produced in all cases (Table 3, entries 1, 3, 4, 5 and 6). Only trace amount of Z isomers (1-2% >) were detected in the crude $^1$H nmr spectra.

## Summary

This presentation describes a fast and facile microwave enhanced *N*-alkenylation synthesis between sulfur-containing lactam and various aldehydes such as *n*-propanal, isopropanal, *n*-butanal, *n*-hexanal, *n*-octanal and phenylacetaldehyde in 32 to 86% yields. In order to explain the conformational properties of *E/Z* isomers, we used the coupling constant (*J*) of $^1$H and 2-D NOESY NMR techniques. In all cases, *E* isomers were predominantly produced. We expect these new *N*-alkenyl pyrrolidine-2-thiones to have interesting applications for the protection of functionalized thiolactams. Consequently, we are currently expanding our results using the advantages of microwave irradiation.

## Experimental Section

Pyrrolidin-2-one, Lawesson's reagent, *p*-toluenesulfonic acid monohydrate (98.5%), bentonite, $K_{10}$, $Al_2O_3$, *n*-propanal, isopropanal, *n*-butanal, *n*-hexanal, *n*-octanal and phenylacetaldehyde were purchased from Sigma-Aldrich (Korea) and used as received. Toluene, chlorobenzene and *m*-xylene were either used as supplied or purified by standard techniques. TLC was performed on precoated glass plate-silica gel 250-$\mu$m (Baker Si250F) with detection by UV light. Flash column chromatography was performed on silica gel (230-400 mesh). The $^1$H and $^{13}$C NMR spectra were recorded at 300 MHz and 75 MHz on a FT-NMR Bruker 300. Chemical shifts are given in ppm and referenced to internal tetramethylsilane (TMS, $\delta$ = 0 ppm) standard. GC/MS spectra were measured on a Shimazu QP 5000 spectrometer.

**Pyrrolidin-2-thione, 3.** To a 500 mL round-bottomed flask equipped with a mechanical stirrer, reflux condenser and a nitrogen line was charged **2** (5.2 g, 61.2 mmol, 1 equiv.), powdered Lawesson's reagent (24.7 g, 61.2 mmol, 1 equiv.) and toluene (200 mL) were added. The mixture was refluxed under $N_2$ atmosphere. After 4 hr, the starting material was determined to be disappeared by TLC analysis (2% MeOH/98% $CH_2Cl_2$). The removal of the solvent using rotary evaporator under reduced pressure and flash column chromatography using 2% MeOH/98% $CH_2Cl_2$ as eluent afforded the product, **3** (4.6 g, 45.9 mmole, 75%) as a solid. mp 112-114 °C (lit[22] 114-115 °C), $^1$H NMR ($CDCl_3$, 300 MHz) $\delta$8.71 (br s, 1H), 3.67 (t, *J* = 7.2 Hz, 2H), 2.84 (t, *J* =

7.9 Hz, 2H), 2.13 (m, 2H). $^{13}$C NMR ($CDCl_3$, 75 MHz) $\delta$ 205.52, 49.73, 43.38 and 22.87 ppm; IR (neat) 3420, 3200, 2952, 1540, 1475 and 1349 $cm^{-1}$.

**The typical experimental procedure for the synthesis of (*E*)-1-(but-1-enyl)pyrrolidine-2-thione, 8** (Table 3, entry 3) is as follows: The reaction vessel containing pyrrolidine-2-thione, **3** (100 mg, 0.99 mmol, 1 equiv.), *n*-butanal (107 mg, 1.49 mmol 1.5 equiv) and 98.5% *p*-toluenesulfonic acid monohydrate (5 mg) in chlorobenzene (10 mL) were placed in a 2450 MHz Samsung microwave oven (model # RE-555 TCW). The mixture was irradiated 5 times for 15 min with 3 min intervals. Additional chlorobenzene (3 mL) was repeatedly provided in the reaction vessel after 3 minutes of microwave irradiation. After completion of the reaction, the mixture was allowed to cool at the room temperature, and the crude product was extracted into $CH_2Cl_2$. The removal of the solvent using rotary evaporator under reduced pressure and flash column chromatography using $CH_2Cl_2$/MeOH (98/2) as eluent afforded the product, **8** (78.2 mg, 0.50 mmol, 51%). $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.49 (1H, d, $J$ = 14.5 Hz), 5.38 (1H, m), 3.79 (2H, t, $J$ = 7.56 Hz), 3.06 (2H, t, $J$ = 7.92 Hz), 2.12 (4H, m) and 1.04 (3H, t, $J$ = 7.41 Hz) $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 199.60, 126.53, 121.36, 52.85, 45.70, 23.83, 19.84 and 14.51 ppm. Infrared (neat): 2962.9-2861.2, 1655.1, 1483.1, 1433.8, 1420.1, 1336.9, 1294.9, 1279.5, 1136.4 and 952.0 $cm^{-1}$. GC/MS 155 ($M^+$, 25), 140 (3), 126 (100), 112(2), 98 (20), 85 (16) and 68 (7). MALDI-TOF-MS m/z calcd for $C_8H_{13}NS$/Exact Mass: 155.0769/found 155.1592.

**(*E*)-1-(Prop-1-enyl)pyrrolidine-2-thione, 6 (Table 3, entry 1)** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.54 (1H, d, $J$ = 13.05 Hz), 5.39 (1H, m), 3.82 (2H, t, $J$ = 7.11 Hz), 3.09 (2H, t, $J$ = 7.74 Hz), 2.12 (2H, m) and 1.80 (3H, d, $J$ = 6.84 Hz). ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 199.51, 126.9, 119.87, 52.64, 45.32, 23 19.61 and 18.02 ppm. GC/MS 141 ($M^+$, 85), 126 (100), 112(12), 98 (58), 85 (25), 71 (32), 56 (50) and 45 (53). FAB MS, m/s 141.3 ($M^+$).

**(*E*)-1-(2-Methylprop-1-enyl)pyrrolidine-2-thione, 7 (Table 3, entry 2)** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 6.27 (1H, s), 3.89 (2H, t, $J$ = 7.29 Hz), 3.04 (2H, t, $J$ = 3.92), 2.58 (1H, m), 1.83 (3H, s) and 1.71 (3H, s) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 199.49, 127.15, 119.61, 52.72, 45.41, 23.01, 19.75 and 18.93 ppm. Infrared (neat): 2971.5-2913.3, 1488.3, 1457.9, 1419.3, 1327.5, 1289.8 and 1130.0 $cm^{-1}$. FAB MS, m/s 155.1 ($M^+$).

**(*E*)-1-(Hex-1-enyl)pyrrolidine-2-thione, 9 (Table 3, entry 4)** $^1$H NMR (300 MHz, $CDCl_3$): 7.48 (1H, d, $J$ = 14.46 Hz), 5.33 (1H, m), 3.79 (2H, t, $J$ = 7.44 Hz), 3.05 (2H, t, $J$ = 7.89 Hz), 2.10 (4H, m), 1.34 (4H, m) and 0.86 (3H, t, $J$ = 6.98 Hz) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 199.44, 127.01, 119.85, 52.85, 45.65, 32.33, 30.21, 22.72, 19.82 and 14.28 ppm. Infrared (neat): 2966.5-2856.7, 1650.3, 1483.2, 1458.5, 1432.4, 1339.5, 1275.6, 1136.9 and 950.9 $cm^{-1}$. FAB MS, m/s 183.2 ($M^+$).

**(*E*)-1-(Oct-1-enyl)pyrrolidine-2-thione, 10 (Table 3, entry 5)** $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.48 (1H, d, $J$ = 14.58 Hz), 5.37 (1H, m), 3.78 (2H, t, $J$ = 7.47 Hz), 3.05 (3H, t, $J$ = 7.74 Hz), 2.08 (4H, m), 1.28 (8H, m) and 0.85 (3H, t) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 199.08, 126.65, 119.47, 52.4115, 45.24, 31.64, 30.15, 29.71, 28.80, 22.57, 19.42, and 14.06 ppm. Infrared (neat): 2966.5-2870.3, 1654.1, 1483.1, 1483.3, 1439.5, 1419.6, 1339.7, 1276.9, 1137.2 and 952.0 $cm^{-1}$. FAB MS, m/s 211.1 ($M^+$).

**(*E*)-1-Styrylpyrrolidine-2-thione, 11 (Table 3, entry 6)** mp 118-120 °C, $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.27 (1H, d, $J$ = 15.03 Hz), 7.33 (5H, m), 6.24 (1H, d, $J$ = 15.03 Hz), 3.97 (2H, t, $J$ = 7.29 Hz), 3.14 (2H, t, $J$ = 8.01 Hz) and 2.12 (2H, m) ppm. $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ 200.76, 135.40, 128.79, 127.61, 126.32, 126.18, 117.68, 52.32, 45.29 and 19.53 ppm. Infrared (neat): 3045.9, 2985.6-2892.0, 1636.3, 1476.7, 1457.4, 1431.9, 1413.0, 134.1, 1287.8, 1258.7, 1136.6, 949.5, 763.0 and 699.4 $cm^{-1}$. FAB MS, m/s 203.1 ($M^+$).

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