Chemoselective Lactam Formation in the Addition of Benzenesulfonyl Bromide to *N*-Allyl Acrylamides and *N*-Allyl 3,3-Dimethylacrylamides

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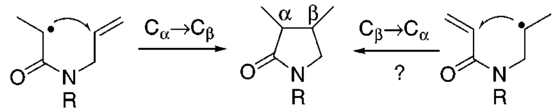
Chemoselectivity in the addition and cyclization reactions of $PhSO_2Br$ to *N*-allyl acrylamides has been confirmed due to the higher reactivity of the acrylic C═C bond toward the sulfonyl radical than that of the allyl C═C bond. Formation of γ-lactams by $C_\beta \rightarrow C_\alpha$ cyclization can be achieved with *N*-allyl 3,3-dimethylacrylamides.

Introduction

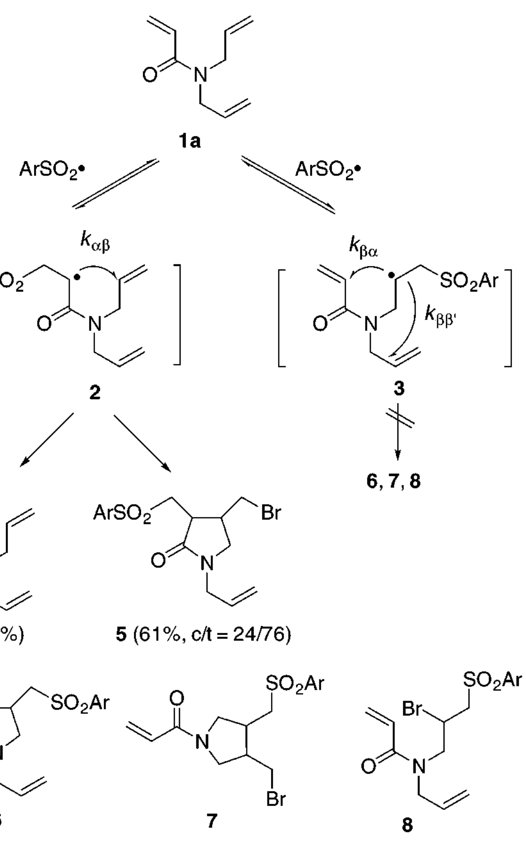
Functionalized γ-lactams are important intermediates in organic synthesis,[1] and many natural products of potential use in medicine and agriculture have a γ-lactam skeleton.[2] Generally, the γ-lactam skeleton is constructed through formation of the acyl-N bond.[3] Recently, formation of the $C_\alpha C_\beta$ bond by Pd-catalyzed[4] or radical[5] cyclizations have received attention. In those radical cyclization reports, the α-carbamoyl radical, generated from the corresponding halide,[5a,b] mercury halide,[5c] or other precursor under thermolysis, photolysis, or mediation of Cu^+, Ni^0, Fe^0, Mn^{3+}, etc., intramolecularly adds to another C═C bond in a 5-exo or 5-endo mode.[5d−g] This kind of cyclization is defined as a $C_\alpha \rightarrow C_\beta$ radical cyclization in this paper (Scheme 1, only exo cyclization is depicted). Surprisingly, we have not found any report of a $C_\beta \rightarrow C_\alpha$ cyclization, which, if possible, would provide a new approach to the γ-lactam skeleton with different functionality.

In fact, $C_\beta \rightarrow C_\alpha$ radical cyclization has been attempted by M. P. Bertrand and his colleagues (Scheme 2).[6] They reported that the reaction of $TolSO_2Br$ with amide **1a** yielded only sulfones **4** and **5**, which originate from radical adduct **2**. Compounds **6**, **7**, and **8**, originating from intermediate **3**, were not found. This result contrasts with what is predicted based on polar effects, because the electrophilic radical $TolSO_2$•, generated by photolysis of $TolSO_2Br$, would be expected to add preferentially to the nucleophilic allyl C═C bond, rather than the electrophilic acrylic C═C bond of **1a**. Bertrand explained this observation by postulating that the initial additions of $TolSO_2$•

Scheme 1



Scheme 2



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Scheme 3

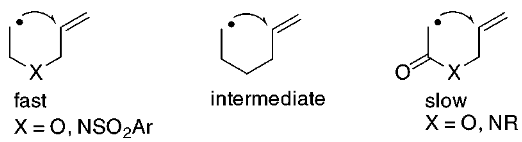


Table 1. Reactions of PhSO$_2$Br and *N*-Allyl Acrylamides under Sunlamp Irradiation in Acetonitrile

amide, R =	products (yield, %)
1a, CH$_2$CH=CH$_2$	**9a** (83, c/t = 1/6.1)
1b, CMe$_3$	**9b** (93, c/t = 1/5.0)
1c, CH$_2$Ph	**9c** (46, c/t = 1/4.6) **10c** (15)
1d, Me	**9d** (50, c/t = 1/2.5) **10d** (41)
1e, Ph	**9e** (25, trans only) **10e** (20)
1f, H	**10f** (46)

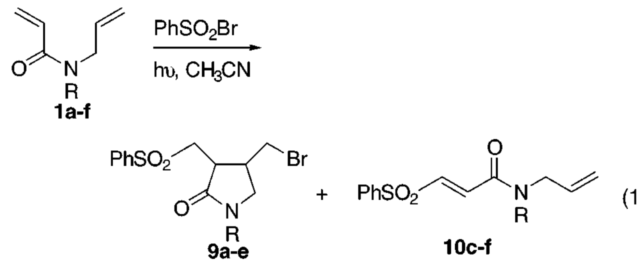
to the acrylic and allyl C=C bonds are reversible, and that the cyclization rate $k_{\alpha\beta}$ is significantly greater than $k_{\beta\alpha}$ and $k_{\beta\beta'}$ (Scheme 2). Since **3** only undergoes slow cyclization processes ($k_{\beta\alpha}$ and $k_{\beta\beta'}$), it can regenerate **1a**, which in turn produces **2** which yields product **5** due to the rapid $k_{\alpha\beta}$ cyclization process and a small amount of uncyclized product **4**.[6a]

Though plausible, Bertrand's explanation has yet to be confirmed. While reversible addition of the sulfonyl radical to C=C bonds has been observed in many cases,[7] there is no report confirming Bertrand's postulate as to the relative rates of $k_{\alpha\beta}$ and $k_{\beta\alpha}$. On the other hand, from the known rates of radical cyclizations which cover 2 orders of magnitude (Scheme 3),[8] we believe that $k_{\alpha\beta}$ is unlikely to be greater than $k_{\beta\beta'}$. Also, Bertrand's explanation could not account for the fact that acrylic C=C bond mono adduct **4** was the only uncyclized product,[6a] and allyl C=C bond mono adduct **8** was not observed. As we see it, even if **3** fails to cyclize ($k_{\beta\alpha}$ and $k_{\beta\beta'}$) to yield **6** and/or **7**, respectively, it could still be intercepted by TolSO$_2$Br to yield **8**.

Thus, we set out to understand the chemoselectivity depicted in Scheme 2 and to try to realize $C_\beta \rightarrow C_\alpha$ radical cyclization. Since the sulfonyl group is a very versatile functional group in organic synthesis[9] and PhSO$_2$• is a stronger electrophilic radical than TolSO$_2$•, we used PhSO$_2$Br to investigate its addition and cyclization reactions with *N*-allyl acrylamides, and *N*-allyl 3,3-dimethyl acrylamides where the $C_\beta \rightarrow C_\alpha$ cyclizations can be enforced by steric effects. In this paper we report our results and rationale.

Results

1. Addition and Cyclization Reactions of PhSO$_2$Br to *N*-Allyl Acrylamides. Table 1 summarizes the reactions of PhSO$_2$Br and *N*-allyl acrylamides (eq 1) under sunlamp irradiation in acetonitrile. Typically, 0.2 M of an amide along with 1.1 equiv of PhSO$_2$Br in acetonitrile was irritiated at room temperature. The uncyclized acrylic C=C bond adducts could not be isolated pure due to their partially dehydrobromination on TLC plates, they were further treated with 2 equiv of triethylamine at rt for about 30 min, and then the dehydrobrominated products **10c**−**f** were isolated by another TLC separation.



The cis/trans configurations of the products **9a**−**e** were determined by 2D NOE, where there is NOE coupling between PhSO$_2$C*H*$_2$ and BrC*H*$_2$ for the cis products, but no coupling is observed for the trans products. This method of assigning the stereochemistry of the products gives the same results as Bertrand's method, where the ^{13}C NMR chemical shift of the cis PhSO$_2$*C*H$_2$ is about 63 ppm, while that of the trans isomer is about 57 ppm. NOE coupling between the two methine H's can be observed in both cis and trans products and therefore cannot be used as a criterion for the stereo configuration assignment. Another possible structure with the groups PhSO$_2$ and Br reversed in products **9** is excluded by HMBC (Heteronuclear Multiple Bond Correlation) 2D spectroscopy. In the HMBC spectrum, one methine H correlates to *C*=O ($\delta \sim 171$ ppm) and PhSO$_2$*C*H$_2$ ($\delta \sim 63$ or 57 ppm), while the other methine H correlates to *C*H$_2$-NR ($\delta \sim 50$ ppm) and Br*C*H$_2$ ($\delta \sim 35$ ppm). Overall, $C_\alpha \rightarrow C_\beta$ cyclization shows trans selectivity.

Table 2. Reactions of PhSO$_2$Br and *N*-Allyl 3,3-Dimethylacrylamides under Sunlamp Irradiation in Acetonitrile

amide, R =	products (yield, %)
11a, CH$_2$CH=CH$_2$	**12a** (34),[a] **13a** (13)[a]
	14 (37, c/t = 2 or 1/2)[b]
11b, CMe$_3$	**12b** (50), **11f** (21)
11c, CH$_2$Ph	**12c** (62), **13c** (37)
11d, Me	**12d** (37),[a] **13d** (15)[a]
11e, Ph	no reaction
11f, H	**15** (72)

[a] Lactams **12a** and **13a**, **12d** and **13d**, are inseparable by TLC; their yields were calculated from the ^{1}H NMR ratio of the two mixtures, respectively. [b] **14** consists of inseparable cis and trans isomers whose ratio was determined by GC-MS without assignment.

2. Addition and Cyclization Reactions of PhSO$_2$Br to *N*-Allyl 3,3-Dimethylacrylamides. We have found that $C_\beta \rightarrow C_\alpha$ cyclizations can be observed in the reactions of PhSO$_2$Br and *N*-allyl 3,3-dimethylacrylamides as shown in Table 2. Addition of 20 mol % Bu$_3$SnSnBu$_3$ was necessary for the complete reaction of amides **11c** and **11d**. $C_\beta \rightarrow C_{\beta'}$ cyclized product **14** was observed from the reaction of amide **11a**. The allyl C=C bond adduct **15** was also observed in the reaction of amide **11f**, and amide **11f** is an unexpected product in the reaction of amide **11b**. There is no reaction for amide **11e**. The trans configuration of lactam **13** were determined by the observed NOE coupling between PhSO$_2$CH$_2$C*H* and BrC(C*H*$_3$)$_2$, and between C*H*CBrMe$_2$ and PhSO$_2$C*H*$_2$.

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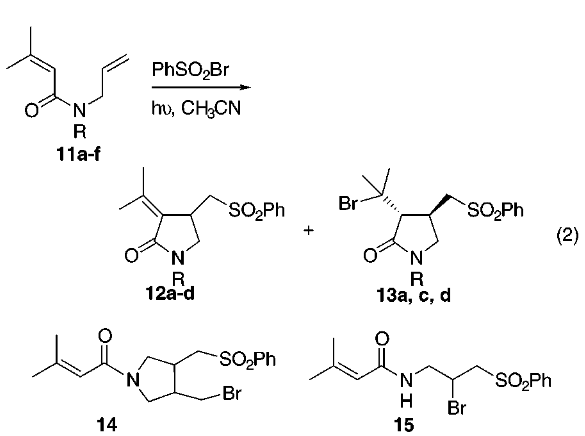
The stereoselectivity of the $C_\beta \rightarrow C_\alpha$ cyclizations cannot be measured, because the cis products, and maybe some trans products, dehydrobrominated readily to yield lactam **12** during TLC separation.



3. Competition Experiments. The relative reactivity of an acrylic C=C bond vs an allyl C=C bond toward $PhSO_2\bullet$ can be quantified by using eqs 3, 4, and 5, where $[M_1]_0$ and $[M_2]_0$ are the initial concentrations of olefins M_1 and M_2, and $[M_1]_t$, $[M_2]_t$ are the concentrations of olefins M_1 and M_2 at time t.[10]

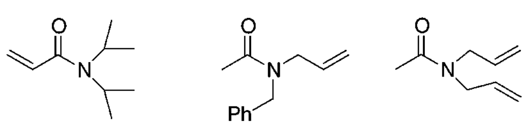
$$PhSO_2\bullet + \begin{cases} M_1 \xrightarrow{k_1} \text{Radical adduct 1} \\ M_2 \xrightarrow{k_2} \text{Radical adduct 2} \end{cases} \quad (3)$$

$$\alpha\,(M_1/M_2) = \{\log[M_1]_0 - \log[M_1]_t\} / \{\log[M_2]_0 - \log[M_2]_t\} \quad (4)$$

$$k_1/k_2 = \alpha\,(M_1/M_2) \quad (5)$$

Equation 5 holds true only if the radical addition step is the rate-determining step and the only step consuming M_1 and M_2. Though reversibility of the radical addition step may complicate the relative reactivity measurement, eq 5 has been shown to be reliable for the addition of $TolSO_2I$ to C=C bonds because of the fast iodo-transfer step following the radical addition step.[10a] The bromo-transfer rate has been estimated to be about one-third that of the iodo-transfer rate from the corresponding benzenesulfonyl halides.[11]

Several reactions were set up in NMR tubes with CD_3CN as the solvent and $(Me_3Si)_2O$ as the internal standard. *N,N*-Diisopropylacrylamide (**16**), *N*-allyl-*N*-benzylacetamide (**17**), *N,N*-diallylacetamide (**18**) were chosen for the measurement of α (**16**/**17**), α (**16**/**18**) (Table 3).



16 **17** **18**

From Table 3, α (**16**/**17**) is about 10, and α (**16**/**18**) only 2.3, much lower than α (**16**/**17**). We believe these two results are consistent. Because there are two allyl C=C bonds in **18**, and every adduct radical intramolecularly cyclizes onto the other allyl C=C bond (Scheme 4), the consuming rate of the allyl C=C bonds of **18** is accelerated roughly by 4 compared to that of **17** if the C=C bond of **18** is as reactive as that of **17**. In this case α (**16**/**18**) should be about one-fourth of α (**16**/**17**), which is very close to the experimental data. Our experiments also showed that in each entry, α was nearly constant within short reaction times, and not affected by either the ratio of the components or the conversion of the reaction, showing the validity of the relative reactivity measurements. So, we believe that in amide **1** the acrylic C=C bond is about 10 times as reactive as the allyl C=C bond toward $PhSO_2\bullet$, and reversibility of the addition of the sulfonyl radical here is not a concern.

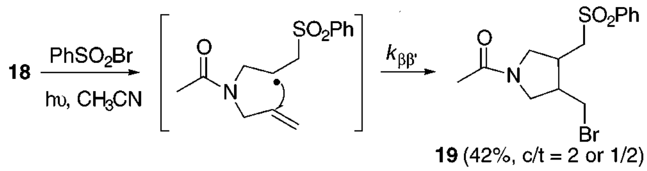
4. Addition and Cyclization Reactions with Other Electrophilic Radicals. Some other electrophilic radicals, such as $CH_3C(O)S\bullet$, $Cl_3C\bullet$, and $(NC)_2CH\bullet$ were also tested in our work (Schemes 5 and 6, and eqs 6 and 7). All of these radicals added only to the acrylic C=C bond, except for amide **11a**.

Table 3. Measurement of α (16/17) and α (16/18)

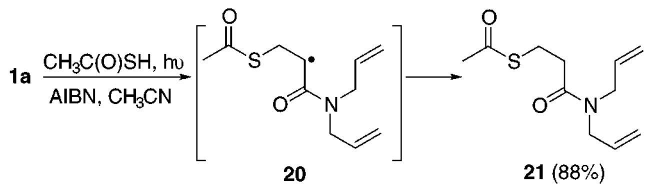
		reaction time (min)			
entry[a]	α (M_1/M_2)	15	30	45	60
1	α (**16**/**17**)	9.5	10.0	8.3	6.8
2	α (**16**/**17**)	10.6	11.0	11.3	8.3
3	α (**16**/**18**)	2.3	2.2	2.0	1.7

[a] Initial molar ratio for entries (by ^{1}H NMR): (1) **16**:**17**:$PhSO_2Br$ = 1.00:1.12:0.90. (2) **16**:**17**:$PhSO_2Br$ = 1.00:1.21:1.27. (3) **16**:**18**:$PhSO_2Br$ = 1.00:1.16:1.70. The concentration of amide **16** was 0.20 M initially for all entries.

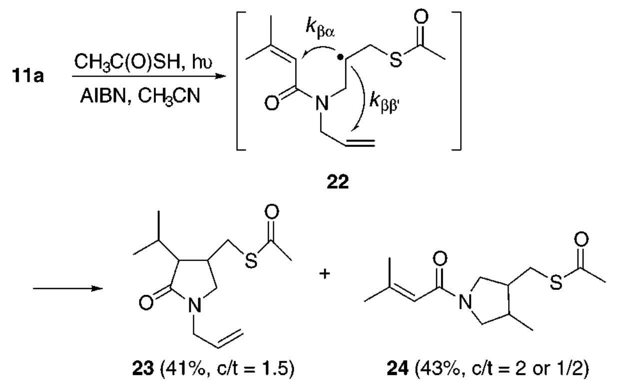
Scheme 4



Scheme 5



Scheme 6



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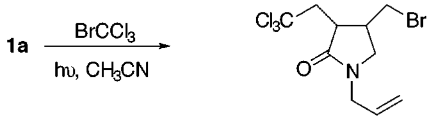
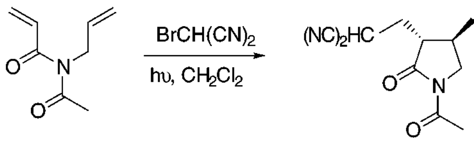


25 (70%, c/t = 1/4) (6)



26 **27** (43%) (7)

Discussion

The results presented in Table 1 are consistent with Bertrand's report. Only $C_\alpha \rightarrow C_\beta$ cyclization processes are observed. The electrophilicity of the sulfonyl radicals does not promote $C_\beta \rightarrow C_\alpha$ cyclization (Scheme 2). Also, the trend in yields of products **9** is consistent with the report that the cis−trans rotamer population of an amide like **1** is controlled by the substituent R (Scheme 7).[6a,12] Amide **1** is about 100% cis-populated when R is *t*-Bu, and 100% trans-populated when R is Ph or H. While the cis rotamer favors the cyclization process, the trans rotamer disfavors this process. The rotation barrier of the C(O)−N bond is about 16−22 kcal/mol,[8a] but it may be lower in the adduct radical.

It is interesting to note that while the uncyclized products **10c**−**f** were generally produced (Table 1), no allyl C═C bond adduct (like **8** shown in Scheme 2) was observed. The result from the reaction of amide **1f** is especially striking: uncyclized product **10f** was the only product isolated. This observation shows that the chemoselectivity here is not related to any cyclization process, and attack on the acrylic C═C bond is strongly preferred to attack on the allyl C═C bond. This conclusion is confirmed by the results of competition experiments.

No cyclized product was observed in the reaction depicted in Scheme 5, which means the rate of $C_\alpha \rightarrow C_\beta$ cyclization of **1a** (or adduct radical **20**) is much slower (about 1 order of magnitude) than that of the H-transfer from $CH_3C(O)SH$ to intermediate **20**. The high yield of cyclized products observed in Scheme 6 suggests that the rates of $C_\beta \rightarrow C_\alpha$ and $C_\beta \rightarrow C_{\beta'}$ cyclizations of amide **11a** (or adduct radical **22**) are much faster (about 1 order of magnitude) than that of the H-transfer from $CH_3C(O)$-SH to intermediate **22**. An analogous observation that the rate of H-transfer from $CH_3C(O)SH$ is slower than that of $C_\beta \rightarrow C_{\beta'}$ cyclization has been reported by Padwa.[13] The rate of H-transfer from $CH_3C(O)SH$ to intermediate **22** should be about the same as that to intermediate **20**, or the former one might be slightly faster because intermediate **20** is more stable than intermediate **22**. From Table 2, the ratio of yields of $k_{\beta\alpha}$ cyclized products (**12a** and **13a**) to $k_{\beta\beta'}$ cyclized product (**14**) is about 1.27. In Scheme 6, this ratio is about 0.95. This shows that the $k_{\beta\beta'}$ for amide **11a**, or more accurately, for the allyl C═C adduct radical of **11a**, is about the same as its $k_{\beta\alpha}$. It is reasonable to suppose the $k_{\beta\beta'}$ for amide **11a** would be about the same as the $k_{\beta\beta'}$ for amide **1a**. Thus, we suggest the following sequence of rates:

$$k_{\beta\alpha}\,(\mathbf{11a}) \sim k_{\beta\beta'}\,(\mathbf{11a}) \sim k_{\beta\beta'}\,(\mathbf{1a}) \gg \text{H-transfer to } \mathbf{22} \sim \text{H-transfer to } \mathbf{20} \gg k_{\alpha\beta} \quad (1a)$$

It is very conservative to say $k_{\beta\beta'}$ (**1a**) is about 100 times greater than $k_{\alpha\beta}$ (**1a**), because the radical cyclization rate has been confirmed to be accelerated by heteroatom (N atom) substitution and decelerated by the presence of a carbonyl group (Scheme 3).[8b,c] Thus, the fact that uncyclized acrylic C═C mono adducts of amides **1** were observed (Table 1), but no uncyclized allyl C═C mono adduct has been seen (Table 2) except for the formation of adduct **15**, suggests that the $C_\beta \rightarrow C_\alpha$ and $C_\beta \rightarrow C_{\beta'}$ cyclization rates of **11a** are faster than the $C_\alpha \rightarrow C_\beta$ cyclization rate of **1a**. No $C_\beta \rightarrow C_{\beta'}$ cyclized product was observed from the reaction of amide **1a** in eq 1 even though $k_{\beta\beta'}$ (**1a**) is greater than $k_{\alpha\beta}$ (**1a**) strongly suggests that Bertrand's assumption is not correct.

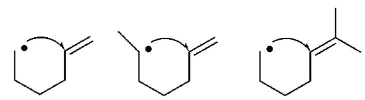
Rate constants $k_{\beta\alpha}$ (**1a**) and $k_{\alpha\beta}$ (**1a**) cannot be compared directly because no product from the former cyclization process is observed, and $k_{\beta\alpha}$ (**1a**) may be different from $k_{\beta\alpha}$ (**11a**). Beckwith reported that the dimethyl groups at the new radical center show little effect on the cyclization rate of 5-hexenyl radicals (Scheme 8).[14] However, in amide **1a**, the acryl C═C bond and C═O bond are conjugated in a planar conformation, and they are not in amide **11a**.[15] The effect of this conformation difference on the rate of cyclizations is difficult to be estimated quantitatively. By guess, we postulate that the difference between $k_{\beta\alpha}$ (**1a**) and $k_{\beta\alpha}$ (**11a**) may be within 1 order of magnitude. As pointed before, $k_{\beta\alpha}$ (**11a**) is about 2 orders of magnitude greater than $k_{\alpha\beta}$ (**1a**). Therefore we think $k_{\beta\alpha}$ (**1a**) may be greater than, or at least comparable with, $k_{\alpha\beta}$ (**1a**).

A significant yield of the cis $C_\beta \rightarrow C_\alpha$ cyclized product was obtained from the reaction of amide **11a** (Scheme 6). However, the $C_\alpha \rightarrow C_\beta$ cyclization gave mainly trans products (eq 1). This observation is also consistent with the general assumption that a fast cyclization process has an early transition state which gives cis-predominant products, while a slow cyclization process has a late transition state which gives trans-predominant products.

In amide **1**, the acrylic C═C bond is about 10 times as reactive as the allyl C═C bond toward a sulfonyl radical as quantified by the competition experiments. This result is unexpected and may be explained by stabilization

Scheme 7

Scheme 8



relative cyclization rates 1 1.4 2.4

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effects due to delocalization of the α-carbamoyl radical over the carbonyl group. Though the relative reactivity of olefins of a homologous series toward a sulfonyl radical is predictable,[6b,10] no general statement could be found to predict the relative reactivity of different olefins such as acrylic and allyl C=C bonds. An acrylic C=C bond of alkyl acrylates was reported as reactive as an allyl C=C bond of alkyl allyl ethers toward a sulfonyl radical.[10c] We also use similar competition experiments to find out that the acrylic C=C bond of **16** is 3 times as reactive as that of ethyl acrylate which is only 1.6 times as reactive as the allyl C=C bond of allyl acetate. The reason for the reactivity difference between acrylamides and acrylates is not clear and may be partially explained as the N atom of acrylamides is less electronegative than the O atom of acrylates.

Other strong electrophilic radicals, such as $Cl_3C•$ and $(NC)_2CH•$, afford only $C_\alpha{\rightarrow}C_\beta$ cyclized products (eqs 6 and 7). Overall, it is unlikely that the electrophilicity of the attacking radical itself can shift the chemoselectivity of addition from an acrylic C=C bond to an allyl C=C bond.

Conclusions

Chemoselectivity in the radical addition and cyclization reactions of $PhSO_2Br$ to *N*-allyl acrylamides is confirmed due to the higher reactivity of the acrylic C=C bond toward the sulfonyl radical than that of the allyl C=C bond. The $C_\beta{\rightarrow}C_\alpha$ cyclization can be observed with *N*-allyl 3,3-dimethylacrylamides, which shows a different stereoselectivity from that of the $C_\alpha{\rightarrow}C_\beta$ cyclization.

Experimental Section

IR spectra were measured as thin films on NaCl plate. NMR spectra were recorded in $CDCl_3$ or as stated otherwise (^1H at 400 MHz and ^{13}C at 100 MHz). All mp's were determined without correction. Photostimulated reactions utilized a 275 W fluorescent sunlamp and 5 mm NMR tubes. Yields were based on the starting acrylamides. $PhSO_2Br$ was prepared according to a literature procedure.[16] Amides **1a**–**f**, **11a**–**f**, **16**, **17**, **18** were prepared from the appropriate acyl chlorides and corresponding amines according to a literature procedure.[6a]

General Procedure for the Addition of $PhSO_2Br$ to Amides. A mixture of an amide (0.20 mmol) and $PhSO_2Br$ (0.22 mmol) in 1.0 mL of CH_3CN was irradiated in a 5 mm NMR tube at room temperature until the starting amide disappeared as indicated by TLC analysis. The products were obtained by TLC separation on 20 × 10 cm silica gel plates with hexanes–ethyl acetate as the eluent. Procedures for reactions depicted in Scheme 5, eqs 6 and 7 are similar except using thioacetic acid together with 10 mol % AIBN, bromotrichloromethane, or bromodicyanomethane instead of using $PhSO_2Br$.

***N*-Allyl-4-(bromomethyl)-3-[(phenylsulfonyl)methyl]-2-pyrrolidone (9a).** The trans isomer was isolated as a yellow oil. IR (cm^{-1}) 1689, 1307, 1151; ^1H NMR δ (C_6D_6) 2.24–2.34 (m, 1H), 2.62 (t, J = 9.6 Hz, 1H), 2.65 (dd, J = 3.0, 9.6 Hz, 1H), 2.69 (ddd, J = 2.0, 9.2, 9.6 Hz, 1H), 2.89 (dd, J = 8.8, 9.6 Hz, 1H), 3.25 (dd, J = 8.4, 10.0 Hz, 1H), 3.48 (dd, J = 6.0, 15.2 Hz, 1H), 3.66 (dd, J = 6.0, 15.2 Hz, 1H), 3.73 (dd, J = 2.0, 9.6 Hz, 1H), 3.81 (dd, J = 3.6, 10.0 Hz, 1H), 4.88 (dd, J = 1.0, 16.8 Hz, 1H), 4.92 (dd, J = 1.0, 10.0 Hz, 1H), 5.42 (ddt, J = 10.0, 16.8, 6.0 Hz, 1H), 6.80–7.70 (m, 5H); ^{13}C NMR δ 35.81, 39.67, 41.66, 45.89, 50.13, 57.72, 119.03, 128.18, 129.70, 131.65, 134.33, 139.23, 171.52; HREIMS *m/z* (relative intensity) 371.0179 (62, calcd for $C_{15}H_{18}{}^{79}BrNO_3S$ 371.0191), 292 (12), 230 (36), 150 (35), 136 (74), 77 (68), 40 (100).

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The cis isomer was isolated as a yellow solid, mp 135–137 °C. IR (cm^{-1}) 1693, 1305, 1146; ^1H NMR (C_6D_6) δ 2.56 (dd, J = 6.8, 10.0 Hz, 1H), 2.64 (m, 1H), 2.79 (dd, J = 0.8, 10.0 Hz, 1H), 2.99 (dd, J = 12.4, 14.0 Hz, 1H), 3.08 (ddd, J = 1.6, 7.2, 12.4 Hz, 1H), 3.12 (dd, J = 8.0, 10.4 Hz, 1H), 3.38 (dd, J = 3.6, 10.4 Hz, 1H), 3.53 (dd, J = 6.4, 15.2 Hz, 1H), 3.63 (dd, J = 6.4, 15.2 Hz, 1H), 3.80 (dd, J = 1.6, 14.0 Hz, 1H), 4.87 (dd, J = 1.2, 17.6 Hz, 1H), 4.90 (dd, J = 1.2, 10.4 Hz, 1H), 5.44 (ddt, J = 10.4, 17.6, 6.4 Hz, 1H), 6.82–7.67 (m, 5H); ^{13}C NMR δ 33.48, 35.54, 40.41, 45.95, 49.63, 52.68, 119.27, 128.15, 129.78, 131.92, 134.40, 139.07, 170.70; HREIMS *m/z* (relative intensity) 371.0184 (53, calcd for $C_{15}H_{18}{}^{79}BrNO_3S$ 371.0191), 292 (24), 230 (59), 150 (34), 136 (76), 77 (58), 40 (100).

***N-tert*-Butyl-4-(bromomethyl)-3-[(phenylsulfonyl)methyl]-2-pyrrolidone (9b)** was isolated as a 1:5 mixture of cis and trans isomers (from ^1H NMR). Only the major isomer (assigned as trans by NOESY spectrum) can be assigned from the ^1H NMR spectrum of the mixture. ^1H NMR (C_6D_6) δ 1.18 (s, 9H), 2.18–2.28 (m, 1H), 2.58 (dd, J = 10.0, 14.0 Hz, 1H), 2.66 (ddd, J = 2.0, 10.0, 14.0 Hz, 1H), 2.72 (dd, J = 5.6, 10.0 Hz, 1H), 3.12 (dd, J = 6.0, 10.0 Hz, 1H), 3.26 (dd, J = 8.4, 10.0 Hz, 1H), 3.75 (dd, J = 2.0, 14.0 Hz, 1H), 3.89 (dd, J = 3.6, 10.0 Hz, 1H), 6.85–7.75 (m, 5H); ^{13}C NMR δ the trans isomer 27.74, 35.76, 39.46, 42.88, 49.12, 54.98, 57.89, 128.09, 129.62, 134.20, 139.36, 171.61; the cis isomer 27.79, 33.34, 35.05, 41.69, 48.35, 52.77, 54.90, 128.03, 129.71, 134.28, 139.16, 170.60; HREIMS *m/z* (relative intensity) 387.0502 (42, calcd for $C_{16}H_{22}{}^{79}BrNO_3S$ 387.0504), 332 (29), 230 (100), 192 (33), 190 (34), 77 (10), 57 (27).

***N*-Benzyl-4-(bromomethyl)-3-[(phenylsulfonyl)methyl]-2-pyrrolidone (9c).** The trans isomer was isolated as a light yellow oil. IR (cm^{-1}) 1691, 1307, 1151; ^1H NMR δ 2.80–2.90 (m, 1H), 2.98 (ddd, J = 2.8, 9.6, 10.0 Hz, 1H), 3.17 (dd, J = 7.6, 10.0 Hz, 1H), 3.18 (dd, J = 10.0, 14.4 Hz, 1H), 3.44 (dd, J = 8.4, 10.0 Hz, 1H), 3.70 (dd, J = 7.2, 10.4 Hz, 1H), 3.85 (dd, J = 2.8, 14.4 Hz, 1H), 3.90 (dd, J = 3.2, 10.4 Hz, 1H), 4.40 (d, J = 14.8 Hz, 1H), 4.48 (d, J = 14.8 Hz, 1H), 7.20–8.10 (m, 10H); ^{13}C NMR δ 35.70, 39.62, 41.64, 47.30, 50.00, 57.68, 128.12, 128.16, 128.33, 129.05, 129.70, 134.33, 135.63, 139.25, 171.79; HREIMS *m/z* (relative intensity) 421.0345 (43, calcd for $C_{19}H_{20}{}^{79}BrNO_3S$ 421.0347), 252 (66), 250 (64), 186 (26), 91 (100).

The cis isomer was isolated as a white solid, mp 118–120 °C. IR (cm^{-1}) 1692, 1305, 1150; ^1H NMR (C_6D_6) δ 2.52 (dd, J = 6.4, 10.0 Hz, 1H), 2.57 (m, 1H), 2.73 (dd, J = 0.4, 10.0 Hz, 1H), 3.00 (dd, J = 12.4, 14.4 Hz, 1H), 3.07 (dd, J = 8.0, 10.4 Hz, 1H), 3.15 (ddd, J = 2.0, 7.6, 12.4 Hz, 1H), 3.32 (dd, J = 3.2, 10.4 Hz, 1H), 3.85 (dd, J = 2.0, 14.4 Hz, 1H), 4.00 (d, J = 14.4 Hz, 1H), 4.30 (d, J = 14.4 Hz, 1H), 7.25–8.10 (m, 10H); ^{13}C NMR δ 33.33, 35.57, 40.42, 47.41, 49.65, 52.71, 128.15, 128.16, 128.63, 129.03, 129.80, 134.42, 135.71, 139.09, 170.95; HREIMS *m/z* (relative intensity) 421.0347 (17, calcd for $C_{19}H_{20}{}^{79}BrNO_3S$ 421.0347), 361 (15), 359 (13), 252 (8), 186 (7), 104 (8), 91 (100).

***N*-Methyl-4-(bromomethyl)-3-[(phenylsulfonyl)methyl]-2-pyrrolidone (9d).** The trans isomer was isolated as a colorless oil. IR (cm^{-1}) 1695, 1306, 1151; ^1H NMR (C_6D_6) δ 2.18–2.28 (m, 1H), 2.32 (s, 3H), 2.40 (dd, J = 7.6, 9.6 Hz, 1H), 2.55 (dd, J = 10.0, 12.0 Hz, 1H), 2.57 (ddd, J = 0.4, 8.0, 10.0 Hz, 1H), 2.69 (dd, J = 8.4, 9.6 Hz, 1H), 3.17 (dd, J = 8.8, 10.0 Hz, 1H), 3.74 (dd, J = 0.4, 12.0 Hz, 1H), 3.86 (dd, J = 4.0, 10.0 Hz, 1H), 6.82–7.75 (m, 5H); ^{13}C NMR δ 30.18, 35.79, 39.63, 41.39, 52.67, 57.74, 128.15, 129.67, 134.31, 139.16, 171.72; HREIMS *m/z* (relative intensity) 345.0035(36, calcd for $C_{13}H_{16}{}^{79}BrNO_3S$ 345.0034), 266 (11), 252 (14), 204 (23), 202 (51), 124 (34), 110 (100).

The cis isomer was isolated as a white solid, mp 95–97 °C. IR (cm^{-1}) 1690, 1304, 1149; ^1H NMR (C_6D_6) δ 2.33 (s, 3H), 2.44 (dd, J = 6.4, 10.0 Hz, 1H), 2.53–2.60 (m, 1H), 2.59 (dd, J = 0.8, 10.0 Hz, 1H), 2.98 (ddd, J = 1.2, 6.8, 13.2 Hz, 1H), 3.02 (dd, J = 1.2, 10.4 Hz, 1H), 3.09 (dd, J = 8.0, 10.4 Hz, 1H), 3.35 (dd, J = 3.6, 10.4 Hz, 1H), 3.80 (dd, J = 9.6, 10.4 Hz, 1H), 6.82–7.75 (m, 5H); ^{13}C NMR δ 30.05, 33.68, 35.48, 40.05, 52.22, 52.75, 128.12, 129.77, 134.39, 139.06, 170.98; HREIMS *m/z* (relative intensity) 345.0034 (15, calcd for $C_{13}H_{16}{}^{79}BrNO_3S$

345.0034), 266 (18), 252 (14), 204 (31), 202 (51), 124 (30), 110 (82), 77 (45), 69 (100).

***trans*-*N*-Phenyl-4-(bromomethyl)-3-[(phenylsulfonyl)-methyl]-2-pyrrolidone (9e)** was isolated as a yellow solid, mp 105−107 °C. IR (cm^{-1}) 1700, 1307, 1151; ^{1}H NMR δ 2.90−3.10 (m, 1H), 3.12 (ddd, J = 2.4, 9.0, 9.6 Hz, 1H), 3.28 (dd, J = 9.6, 14.1 Hz, 1H), 3.78 (dd, J = 7.8, 8.4 Hz, 1H), 3.81 (dd, J = 7.5, 10.5 Hz, 1H), 3.90 (dd, J = 2.4, 14.1 Hz, 1H), 4.01 (dd, J = 8.4, 10.0 Hz, 1H), 4.06 (dd, J = 3.6, 10.5 Hz, 1H), 7.10−8.00 (m, 10H); ^{13}C NMR δ 35.16, 39.43, 42.87, 51.84, 57.56, 120.31, 125.58, 128.23, 129.24, 129.75, 134.41, 138.68, 139.21, 170.96; HREIMS *m/z* (relative intensity) 407.0187 (51, calcd for $C_{18}H_{18}{}^{79}BrNO_3S$ 407.0191), 268 (98), 266 (100), 186 (37), 172 (56), 104 (26), 77 (64).

***N*-Benzyl-*N*-(2-propenyl)-3-(phenylsulfonyl)acrylamide (10c)** was isolated as a colorless oil. IR (cm^{-1}) 1653, 1320, 1148; ^{1}H NMR (2 rotamers) δ 3.95 (d, J = 4.8, 1.2H), 4.06 (d, J = 6.0 Hz, 0.8H), 4.62 (s, 0.8H), 4.65 (s, 1.2H), 5.15−5.35 (m, 2H), 5.7−5.9 (m, 2H), 7.15−7.95 (m, 10H); ^{13}C NMR δ (2 rotamers, * for overlapping peaks) 48.97, 49.49, 49.64, 50.73, 118.12, 118.93, 126.75*, 128.06, 128.31, 128.36, 128.41, 128.57, 128.99, 129.37, 129.72, 129.76, 131.29, 132.01, 132.26, 134.32, 134.37, 135.98, 136.55, 138.99, 139.06, 141.86, 141.68, 163.31, 163.56; HREIMS *m/z* (relative intensity) 341.1081 (25, calcd for $C_{19}H_{19}NO_3S$ 341.1086), 300 (41), 200 (72), 146 (43), 125 (58), 106 (69), 91 (100), 77 (29).

***N*-Methyl-*N*-(2-propenyl)-3-(phenylsulfonyl)acrylamide (10d)** was isolated as a yellow oil. IR (cm^{-1}) 1651, 1321, 1151; ^{1}H NMR (2 rotamers) δ 3.01 (s, 1.7H), 3.09 (s, 1.3H), 4.00−4.10 (m, 2H), 5.13−5.30 (m, 2H), 5.65−5.88 (m, 1H), 7.28 (d, J = 14.7 Hz, 1H), 7.43 (d, J = 14.7 Hz, 1H), 7.55−7.95 (m, 5H); ^{13}C NMR (2 rotamers) δ 34.56, 35.27, 50.80, 52.68, 117.88, 118.61, 128.35, 128.37, 129.74, 129.76, 131.13, 131.24, 131.89, 132.08, 134.33, 134.37, 139.05, 139.10, 141.11, 141.37, 162.72, 163.38; HREIMS *m/z* (relative intensity) 265.0769 (36, calcd for $C_{13}H_{15}NO_3S$ 265.0773), 142 (13), 124 (79), 77 (24), 70 (100).

***N*-Phenyl-*N*-(2-propenyl)-3-(phenylsulfonyl)acrylamide (10e)** was isolated as a colorless oil. IR (cm^{-1}) 1653, 1320, 1149; ^{1}H NMR δ 4.36 (d, J = 6.2 Hz, 1H), 5.08−5.17 (m, 2H), 5.85 (ddt, J = 1.2, 10.2, 16.8 Hz, 1H), 6.78 (d, J = 14.7 Hz, 1H), 7.30 (d, J = 14.7 Hz, 1H), 7.13 (m, 2H), 7.40−7.80 (m, 8H); ^{13}C NMR δ 53.06, 119.00, 127.96, 128.31, 128.97, 129.66, 130.19, 132.03, 132.08, 134.24, 139.14, 140.80, 140.95, 162.18; HREIMS *m/z* (relative intensity) 327.0926 (4, calcd for $C_{18}H_{17}NO_3S$ 327.0929), 186 (100), 132 (30), 125 (25), 77 (34).

***N*-(2-Propenyl)-3-(phenylsulfonyl)acrylamide (10f)** was isolated as a white solid, mp 119−121 °C. IR (cm^{-1}) 1653, 1308, 1148; ^{1}H NMR δ 3.96 (m, 2H), 5.17−5.25 (m, 2H), 5.78−5.60 (m, 1H), 5.95−6.05 (br, 1H), 6.94 (d, J = 14.7 Hz, 1H), 7.33 (d, J = 14.7 Hz, 1H), 7.55−7.92 (m, 5H); ^{13}C NMR δ 42.71, 117.82, 128.38, 128.37, 129.80, 133.43, 134.47, 138.97, 140.77, 161.82. HREIMS *m/z* (relative intensity) 251.0619 (35, calcd for $C_{12}H_{13}NO_3S$ 251.0616), 142 (22), 125 (73), 110 (65), 77 (41), 56 (100), 41 (38).

***N*-Allyl-4-[(phenylsulfonyl)methyl]-3-isopropylidene-2-pyrrolidone (12a)** was isolated as a 2.3:1 mixture with **13a** (from ^{1}H NMR). ^{1}H NMR δ (* for overlapping peaks with **13a**) 1.63 (s, 3H), 2.21 (s, 3H), 3.0−4.2* (m, 7H), 5.21−5.30* (m, 2H), 5.68−5.73* (m, 1H), 7.61−7.95* (m, 5H); ^{13}C NMR δ 19.39, 22.86, 31.17, 45.63, 48.45, 59.95, 118.69, 126.19, 128.19, 129.76*, 132.32, 134.31, 139.37, 144.91, 167.59; HREIMS *m/z* (relative intensity) 319.1242 (57, calcd for $C_{17}H_{21}NO_3S$ 319.1242), 178 (17), 164 (100), 82 (25).

***N*-*tert*-Butyl-4-[(phenylsulfonyl)methyl]-3-isopropylidene-2-pyrrolidone (12b)** was isolated as a white solid, mp 118−120 °C. IR (cm^{-1}) 1681, 1306, 1153; ^{1}H NMR δ 1.39 (s, 9H), 1.58 (s, 3H), 2.17 (s, 3H), 3.00 (dd, J = 1.2, 14.0 Hz, 1H), 3.17 (dd, J = 7.2, 14.0 Hz, 1H), 3.25−3.35 (m, 1H), 3.45 (dd, J = 6.8, 10.8 Hz, 1H), 3.59 (dd, J = 0.8, 10.8 Hz, 1H), 7.61−7.95 (m, 5H); ^{13}C NMR δ 19.22, 22.86, 27.80, 31.05, 46.79, 54.38, 59.63, 127.84, 128.18, 129.75, 134.29, 139.49, 143.39, 168.60; HREIMS *m/z* (relative intensity) 335.1554 (57, calcd for $C_{18}H_{25}NO_3S$ 335.1555), 320 (100), 180 (20), 124 (37).

***N*-Benzyl-4-[(phenylsulfonyl)methyl]-3-isopropylidene-2-pyrrolidone (12c)** was isolated as a yellow oil. IR (cm^{-1}) 1688, 1307, 1147; ^{1}H NMR (C_6D_6) δ 1.24 (s, 3H), 2.33 (s, 3H), 2.50−2.60 (m, 2H), 2.98 (dd, J = 6.8, 10.4 Hz, 1H), 3.10−3.20 (m, 1H), 3.26 (dd, J = 0.8, 10.4 Hz, 1H), 4.14 (d, J = 14.4 Hz, 1H), 4.46 (d, J = 14.4 Hz, 1H), 7.50−7.85 (m, 5H); ^{13}C NMR δ 19.87, 23.12, 31.32, 47.70, 48.88, 59.72, 125.80, 128.08, 128.12, 128.62, 129.05, 129.73, 134.30, 136.00, 139.18, 146.80, 167.96; HREIMS *m/z* (relative intensity) 369.1407 (74, calcd for $C_{21}H_{23}NO_3S$ 369.1399), 228 (19), 214 (72), 91 (100), 83 (30).

***N*-Methyl-4-[(phenylsulfonyl)methyl]-3-isopropylidene-2-pyrrolidone (12d)** was isolated as a 2.5:1 mixture with **13d**. ^{1}H NMR (C_6D_6) δ 1.25 (s, 3H), 2.31 (s, 3H), 2.52 (s, 3H), 2.52−2.60 (m, 2H), 2.87 (dd, J = 6.8, 10.4 Hz, 1H), 3.15−3.22 (m, 1H), 3.27 (dd, J = 0.8, 10.8 Hz, 1H), 6.88−6.95 (m, 3H), 7.60−7.70 (m, 2H); ^{13}C NMR δ 19.24, 22.81, 30.13, 31.06, 50.99, 59.86, 125.99, 128.14, 129.74, 134.30, 139.35, 144.27, 168.08; HREIMS *m/z* (relative intensity) 293.1085 (49, calcd for $C_{15}H_{19}NO_3S$ 293.1086), 138 (100), 84 (58).

***N*-Allyl-3-(1-bromo-1-methylethyl)-4-[(phenylsulfonyl)-methyl]-2-pyrrolidone (13a)** was isolated as a 1:2.3 mixture with **12a** (from ^{1}H NMR). ^{1}H NMR δ (* for overlapping peaks with **12a**) 1.79 (s, 3H), 1.94 (s, 3H), 2.47 (d, J = 3.6 Hz, 1H), 3.0−4.2* (m, 7H), 5.21−5.30* (m, 2H), 5.68−5.73* (m, 1H), 7.61−7.95* (m, 5H); ^{13}C NMR δ 30.42, 31.32, 34.62, 45.77, 50.27, 60.04, 61.74, 67.77, 119.10, 128.26, 129.76*, 131.65, 134.40, 139.23, 169.75; HREIMS *m/z* (relative intensity) 399.0498 (1, calcd for $C_{17}H_{22}{}^{79}BrNO_3S$ 399.0502), 319 (60), 178 (18), 164 (100), 77 (16).

***trans*-*N*-Benzyl-3-(1-bromo-1-methylethyl)-4-[(phenyl-sulfonyl)methyl]-2-pyrrolidone (13c)** was isolated as a yellow oil. IR (cm^{-1}) 1682, 1292, 1146; ^{1}H NMR (C_6D_6) δ 1.65 (s, 3H), 1.85 (s, 3H), 2.05 (d, J = 5.2 Hz, 1H), 2.48 (dd, J = 11.2, 14.0 Hz, 1H), 2.80−2.90 (m, 1H), 2.99 (dd, J = 2.4, 14.0 Hz, 1H), 3.12 (dd, J = 4.0, 10.4 Hz, 1H), 3.44 (dd, J = 8.8, 10.4 Hz, 1H), 3.98 (d, J = 14.4 Hz, 1H), 4.44 (d, J = 14.4 Hz, 1H), 6.80−7.85 (m, 10H); ^{13}C NMR δ 30.47, 31.31, 34.66, 47.23, 50.15, 59.98, 61.72, 67.78, 128.11, 128.24, 128.57, 129.03, 129.72, 134.37, 135.86, 139.10, 169.97; HREIMS *m/z* (relative intensity) 369.1408 [59, calcd for $C_{21}H_{23}NO_3S$ (M − HBr) 369.1399], 228 (19), 214 (69), 91 (100); CIMS *m/z* 469/467 (M + NH_4^+).

***trans*-*N*-Methyl-3-(1-bromo-1-methylethyl)-4-[(phenyl-sulfonyl)methyl]-2-pyrrolidone (13d)** was isolated as a 1:2.5 mixture with **12d**. ^{1}H NMR (C_6D_6) δ 1.62 (s, 3H), 1.86 (s, 3H), 2.40 (s, 3H), 1.98 (d, J = 5.6 Hz, 1H), 2.52 (dd, J = 12.0, 14.0 Hz, 1H), 2.78−2.85 (m, 1H), 2.98 (dd, J = 4.4, 10.4 Hz, 1H), 3.05 (dd, J = 2.8, 14.0 Hz, 1H), 3.33 (dd, J = 8.8, 10.4 Hz, 1H), 6.88−6.95 (m, 3H), 7.60−7.70 (m, 2H); ^{13}C NMR δ 30.05, 31.31, 31.34, 34.89, 52.69, 59.80, 61.66, 67.89, 128.22, 129.74, 134.38, 139.12, 170.04; HREIMS *m/z* (relative intensity) 293.1085 [49, calcd for $C_{15}H_{19}NO_3S$ (M − HBr) 293.1086], 138 (100), 84 (58); CIMS *m/z* 376/374 (M + H$^+$).

***N*-(3,3-Dimethylacryloyl)-3-(bromomethyl)-2-[(phenyl-sulfonyl)methyl]pyrrolidine (14)** was isolated as a 1:2 or 2:1 (from GC-MS) mixture of cis and trans isomers without assignment. ^{1}H NMR δ 1.88 (s, 3H), 2.10 (s, 3H), 2.5−4.0 (m, 10H), 5.76 (s, 1H), 7.61−7.95 (m, 5H); ^{13}C NMR δ major isomer 20.41, 27.36, 30.36, 36.33, 42.39, 48.80, 50.25, 54.14, 116.94, 128.18, 129.82, 134.43, 139.20, 151.45, 166.75; minor isomer 20.43, 27.38, 30.36, 35.06, 43.58, 48.80, 50.82, 54.67, 116.91, 128.18, 129.82, 134.43. 139.14, 151.31, 166.70; HREIMS *m/z* (relative intensity) 399.0502 (40, calcd for $C_{17}H_{22}{}^{79}BrNO_3S$ 399.0504), 320 (19), 318 (37), 246 (57), 176 (28), 83 (100), 55 (16).

***N*-[(2-Bromo-3-phenylsulfonyl)propyl]-3,3-dimethyl-acrylamide (15)** was isolated as a light yellow solid, mp 130−132 °C. IR (cm^{-1}) 1650, 1308, 1146; ^{1}H NMR δ 1.86 (s, 3H), 2.16 (s, 3H), 3.60−3.80 (m, 4H), 4.43 (pentet, J = 6.0 Hz, 1H), 5.59 (s, 1H), 5.88−5.93 (b, 1H), 7.50−8.10 (m, 5H); ^{13}C NMR δ 20.18, 27.47, 43.48, 45.27, 61.78, 117.88, 128.52, 129.70, 134.48, 139.18, 152.21, 167.08; HREIMS *m/z* (relative intensity) 279.0924 [22, calcd for $C_{14}H_{17}NO_3S$ (M − HBr) 279.0929], 138 (97), 83 (100), 55 (20); CIMS *m/z* 379/377 (M + NH_4^+).

***N*-Acetyl-3-(bromomethyl)-2-[(phenylsulfonyl)methyl]-pyrrolidine (19)** was isolated as a 1:2 or 2:1 (from GC-MS) mixture of cis and trans isomers without assignment. ^{1}H NMR

δ 2.07 (s, 3H), 2.50−4.00 (m, 10H), 7.50−8.10 (m, 5H); ^{13}C NMR δ major isomer 22.47, 29.91, 36.27, 42.62, 49.05, 50.71, 53.92, 128.17, 129.86, 134.50, 139.22, 169.87; HREIMS *m*/*z* (relative intensity) 359.0188 (16, calcd for $C_{14}H_{18}{}^{79}BrNO_3$ 359.0191), 318 (19), 316 (17), 224 (19), 204 (100), 176 (48), 137 (18), 96 (58), 77 (47), 43 (99).

***N*,*N*-Diallyl-3-(acetylthio)propionamide (21)** was isolated as a colorless oil. IR (cm^{-1}) 1694, 1651; ^{1}H NMR δ 2.30 (s, 3H), 2.62 (t, *J* = 6.6 Hz, 2H), 3.15 (t, *J* = 6.6 Hz, 2H), 3.83 (d, *J* = 4.8 Hz, 2H), 3.97 (d, *J* = 6.0 Hz, 2H), 5.10−5.20 (m, 4H), 5.75−5.85 (m, 2H); ^{13}C NMR δ 24.99, 30.68, 33.31, 48.23, 49.09, 116.87, 117.65, 132.66, 133.26, 171.00, 196.54; HREIMS *m*/*z* (relative intensity) 227.0984 (16, calcd for $C_{11}H_{17}BNO_2S$ 227.0980), 184 (47), 152 (49), 124 (45), 96 (25), 70 (21), 56 (87), 43 (99), 41 (100).

***N*-Allyl-3-(1-methylethyl)-4-[(acetylthio)methyl]-2-pyrrolidone (23).** The trans isomer was isolated as a colorless oil. IR (cm^{-1}) 1694; ^{1}H NMR δ 0.90 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 2.18 (dd, *J* = 4.4, 4.8 Hz, 1H), 2.22−2.27 (m, 1H), 2.30−2.40 (m, 1H), 2.35 (s, 3H), 2.91 (t, *J* = 13.2 Hz, 1H), 2.93 (dd, *J* = 4.8, 10.4 Hz, 1H), 3.06 (dd, *J* = 5.6, 13.2 Hz, 1H), 3.44 (dd, *J* = 8.4, 10.4 Hz, 1H), 3.79 (dd, *J* = 6.0, 15.2 Hz, 1H), 3.95 (dd, *J* = 6.0, 15.2 Hz, 1H), 5.10−5.20 (m, 2H), 5.69 (ddt, *J* = 9.6, 17.6, 6.0 Hz, 1H); ^{13}C NMR δ 18.46, 20.27, 29.23, 30.87, 32.97, 34.66, 45.36, 50.87, 54.05, 118.31, 132.53, 174.87, 195.46; HREIMS *m*/*z* (relative intensity) 255.1294 (27, calcd for $C_{13}H_{21}NO_2S$ 255.1293), 212 (37), 180 (16), 166 (7), 136 (12), 124 (100), 83 (28), 55 (10), 43 (32).

The cis isomer was isolated as a colorless oil. IR (cm^{-1}) 1699; ^{1}H NMR δ 1.11 (d, *J* = 6.8 Hz, 3H), 1.15 (d, *J* = 6.8 Hz, 3H), 2.00 (octet, *J* = 6.8 Hz, 1H), 2.31 (dd, *J* = 6.8, 8 Hz, 1H), 2.35 (s, 3H), 2.50−2.60 (m, 1H), 2.82 (dd, *J* = 13.6 Hz, 14.0, 1H), 3.02 (dd, *J* = 5.6, 10.0 Hz, 1H), 3.13 (dd, *J* = 4.8, 13.6 Hz, 1H), 3.30 (dd, *J* = 7.2, 10.0 Hz, 1H), 3.83 (dd, *J* = 6.4, 15.2 Hz, 1H), 3.92 (dd, *J* = 6.4, 15.2 Hz, 1H), 5.15−5.25 (m, 2H), 5.70 (ddt, *J* = 10.0, 17.2, 6.4 Hz, 1H); ^{13}C NMR δ 20.01, 22.46, 26.78, 28.40, 30.83, 36.75, 45.40, 50.13, 51.27, 118.47, 132.76, 174.51, 195.48; HREIMS *m*/*z* (relative intensity) 255.1296 (26, calcd for $C_{13}H_{21}NO_2S$ 255.1293), 213 (28), 180 (8), 166 (26), 136 (15), 124 (100), 83 (14), 43 (32).

***N*-(3,3-Dimethylacryloyl)-4-methyl-3-[(acetylthio)methyl]pyrrolidine (24)** was isolated as a 2: 1 or 1:2 (from GC-MS) mixture of cis and trans isomers without assignment. ^{1}H NMR δ 0.96 (d, *J* = 6.8 Hz, 3H, minor isomer), 1.06 (d, *J* = 6.4 Hz, 3H, major isomer), 1.82 (s, 3H), 2.03 (s, 3H), 2.31 (s, 3H), 2.70−4.00 (m, 8H), 5.71 (s, *J* = 10.0 Hz, 1H); HREIMS *m*/*z* (relative intensity) 255.1296 (27, calcd for $C_{13}H_{21}NO_2S$ 255.1293), 212 (5), 166 (33), 130 (10), 83 (100), 55 (18), 43 (10).

***N*-Allyl-4-(bromomethyl)-3-(2,2,2-trichloroethyl)-2-pyrrolidone (25).** A 1:4 mixture of cis and trans isomers were found by GC-MS. Only the trans isomer was isolated pure as a yellow oil. IR (cm^{-1}) 1695; ^{1}H NMR (C_6D_6) δ 1.90−1.99 (m, 1H), 2.17 (dd, *J* = 7.6, 11.2 Hz, 1H), 2.31 (dt, *J* = 3.2, 7.6 Hz, 1H), 2.57 (dd, *J* = 7.2, 9.6 Hz, 1H), 2.73 (t, *J* = 10.0 Hz, 1H), 2.86 (dd, *J* = 8.0, 9.6 Hz, 1H), 3.24 (dd, *J* = 3.6, 10.0 Hz, 1H), 3.42 (dd, *J* = 3.2, 11.2 Hz, 1H), 3.55−3.67 (m, 2H), 4.88−4.95 (m, 2H), 5.47 (ddt, *J* = 10.8, 16.8, 6.0 Hz, 1H); ^{13}C δ NMR 35.79, 40.03, 45.68, 45.89, 50.19, 56.08, 98.70, 119.02, 131.86, 172.70; HREIMS *m*/*z* (relative intensity) 346.9243 (12, calcd for $C_{10}H_{13}{}^{79}Br^{35}Cl_3NO$ 346.9246), 314 (8), 217 (16), 122 (80), 68 (100).

Preparation of *N*-Acetyl-*N*-allylacrylamide (26). To the solution of NaH (240 mg) in anhydrous ethyl ether (10 mL) cooled to 0 °C was added dropwise *N*-allylacrylamide (220 mg, 2 mmol). After the gaseous bubbling subsided, the solution was stirred for another 10 min, acryloyl chloride (0.32 mL, 4 mmol) was added dropwise, and stirring was continued another 30 min. Then the solution was hydrolyzed by cautious addition of water, extracted with ether, and dried over $MgSO_4$. Purification by column chromatography on silica gel gave a light yellow liquid of **26** (200 mg, 65%). IR (cm^{-1}) 1703, 1694; ^{1}H NMR δ 2.46 (s, 3H), 4.36 (d, *J* = 4.8 Hz, 2H), 5.14 (dd, *J* = 0.8, 16.4 Hz, 1H), 5.21 (dd, *J* = 0.8, 10.4 Hz, 1H), 5.80 (dd, *J* = 1.6, 10.4 Hz, 1H), 5.88 (ddt, *J* = 10.4, 16.4, 4.8 Hz, 1H), 6.43 (dd, *J* = 1.6, 16.8 Hz, 1H), 6.73 (dd, *J* = 10.4, 16.8 Hz, 1H); ^{13}C NMR δ 26.30, 46.70, 116.72, 130.53, 130.57, 133.00, 168.94, 173.39; HREIMS *m*/*z* (relative intensity) 153.0790 (11, calcd for $C_8H_{11}NO$ 153.0790), 111 (32), 98 (28), 55 (100), 43 (61).

***N*-Acetyl-4-(bromomethyl)-3-(2,2-dicyanoethyl)-2-pyrrolidone (27)** was isolated as a light yellow oil. IR (cm^{-1}) 2260, 1729, 1704; ^{1}H NMR δ 2.31 (ddd, *J* = 4.8, 10.8, 14 Hz, 1H), 2.40−2.46 (m, 1H), 2.47 (ddd, *J* = 10.8, 11.2, 14.0 Hz, 1H), 2.50 (s, 3H), 2.87 (dt, *J* = 3.6, 10.8 Hz, 1H), 3.47 (dd, *J* = 9.2, 12.0 Hz, 1H), 3.52 (dd, *J* = 6.0, 10.8 Hz, 1H), 3.61 (dd, *J* = 4.4, 10.8 Hz, 1H), 4.12 (dd, *J* = 8.4, 12.0 Hz, 1H), 4.86 (dd, *J* = 4.8, 11.2 Hz, 1H); ^{13}C NMR δ 20.27, 25.27, 31.11, 32.11, 38.26, 44.34, 47.69, 112.18, 112.50, 170.50, 174.39; HREIMS *m*/*z* (relative intensity) 297.0113 (5, calcd for $C_{11}H_{12}{}^{79}BrN_3O_2$ 297.0113), 271 (2), 258 (2), 221 (2), 175 (2), 139 (2), 126 (3), 84 (2), 42 (100).

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Supporting Information Available: ^{1}H, ^{13}C NMR, and 2D ^{1}H−^{1}H NOESY spectra for compounds **9a**−**e**, the mixture of **12a** and **13a**, the mixture of **12d** and **13d**, **13c**, **23**, **25** and **27**; ^{1}H and ^{13}C NMR spectra for compounds **10c**−**f**, **12b**−**c**, **14**, **15**, **19** and **21**; ^{1}H NMR spectrum for compound **24**. This material is available free of charge via the Internet at http://pubs.acs.org.

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