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Tetrahedron 62 (2006) 4188–4200
Tetrahedron

'Push–Pull' and spirobicyclic structures by reacting *N*-methyl cyclic ketene-*N*,X (X = S, O)-acetals with isocyanates and isothiocyanates

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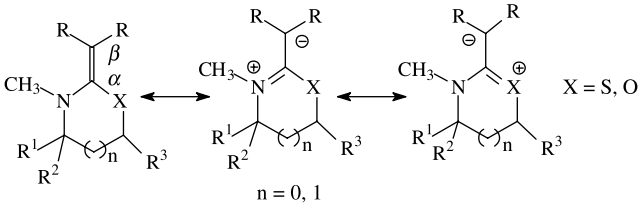
Received 3 October 2005; revised 27 January 2006; accepted 2 February 2006

Available online 10 March 2006

Abstract—Nucleophilic *N*-methyl cyclic ketene-*N*,X (X = S, O)-acetals can react with electrophilic aryl isocyanates and aryl isothiocyanates to form 'push–pull' mono-adducts, di-adducts and spirobicyclic 6/5 ring compounds.

1. Introduction

N-Methyl cyclic ketene-*N*,X (X = S, O)-acetals are electron-rich nucleophilic agents, which have the ability to react with electron deficient electrophiles.[1–8] *N*-Methyl cyclic ketene-



Scheme 1.

N,X (X = S, O)-acetals exhibit extremely electron-rich double bonds with highly polarized exocyclic β carbon atoms (β position is defined in Scheme 1), due to their dual character as both an enamine and a vinyl ether (or vinyl thioether). The electron-rich double bonds of cyclic ketene (*O*,*O*-, *N*,*O*- and *N*,*S*-)-acetals can be easily protonated by protons from moisture and acids.[1]

The earliest report of acyclic ketene-*O*,*N*-acetal, which we are aware of appeared in McElvain's 1949 review.[2] Subsequently, others described the use of acyclic and cyclic ketene-*N*,*O*-acetals as reactants or reaction intermediates.[3–17] In contrast to acyclic and cyclic ketene-*N*,*O*-acetals, only a few reports exist concerning the syntheses and uses of acyclic or cyclic ketene-*N*,*S*-acetals.[18–22] Hiroki first demonstrated the reaction of acyclic ketene-*N*,*S*-acetals with phenyl isocyanate.[19,20] Later, Endo briefly reported the reactions of cyclic ketene-*N*,*O*-acetals with phenyl isocyanate[11] and thioisocyanate.[8] Other than these few reports, no detailed studies of these nucleophiles have appeared. Therefore, our laboratory has undertaken a general investigation of cyclic ketene acetal polymerization[23,25] and reactions with electrophiles and dielectrophiles.[22,24,26–29] Unique cyclizations to fused heterocyclic ring systems and high yield ring-opening reactions suitable for combinatorial applications have been observed.[31] Since a more complete exploration of these reactions is needed, we explored the reactions of aryl isocyanates and aryl isothiocyanates with various cyclic ketene-*N*,*O*-acetals at different temperatures. Cyclic ketene-*N*,*S*-acetals were synthesized and their reactions with isocyanates and thioisocyanates were also studied.

An important capability of both ketene-*N*,*O*- and -*N*,*S*-acetals is the ability to regenerate the acetal double bond by elimination of a proton after addition of the β-carbon to an electrophile gives the resulting zwitterion. Thus, a new ketene acetal function is available for further reaction. This opens many synthetic possibilities,[22,24,26–28] such as cyclization with diacid chlorides[28] and chlorocarbonyl isocyanate.[27]

2. Results and discussion

The detailed syntheses of *N*-methyl cyclic ketene-*N*,X-acetals **1** (X = S), **2** and **3** (X = O) can be easily found in our previous papers and dissertations.[22–30] The three classes of *N*-methyl

Keywords: Enamine; Isocyanates and thioisocyanates; Nucleophilic agents; Ketene-*O*, *N*-acetals; Ketene-*O*, *S*-acetals.
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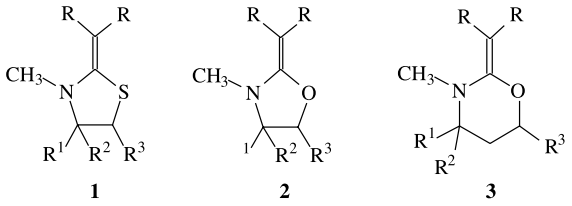
doi:10.1016/j.tet.2006.02.011



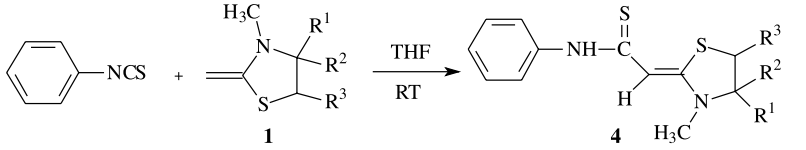
Scheme 2.

cyclic ketene-*N*,X (X=S, O)-acetals represented in structures **1–3** (Scheme 2) were synthesized in this research. These *N*-methyl cyclic ketene-*N*,X (X=S, O)-acetals are all very sensitive to acid and water. Protonation at the exocyclic β-carbon readily generates the corresponding stable heterocyclic cations, which readily react with water. Since the β-carbon is nucleophilic, we explored the reactions of **1–3** with electrophilic isocyanates and isothiocyanates.

N-Methyl cyclic ketene-*N*,*S*-acetals reacted readily with phenyl isothiocyanate at ambient temperature in THF via nucleophilic attack at the electron-deficient isothiocyanate carbon. For example, the four *N*-methyl-2-methylene-1,3-thiazolanes **1a–d** afforded excellent isolated yields of the α,β-unsaturated thioamide monoadducts **4a–d** (Scheme 3). In these substituted 2-(3-methylthiazolidin-2-ylidene)-*N*-phenylthioacetamides, the strong electron-donating enamine and thiovinyl ether functions are conjugated to the electron-withdrawing thioamide function to form a 'push–pull' conjugated system. NOESY experiments proved that the vinyl proton in **4** was cis to the ring nitrogen, because there is a cross-peak between the vinyl proton and protons of the *N*-methyl group. This requires that these protons are spatially near each other, confirming the cis geometry.

Both five- and six-membered ring *N*-methyl cyclic ketene-*N*,*O*-acetals **2** and **3** also react with aryl isothiocyanates to generate monoadducts **5** and **6**, respectively (Scheme 4). For example, 2-methylene-*N*-methyl-1,3-oxazolanes **2a–b** and 3,4,4,6-tretamethyl-2-methylene-1,3-oxazine **3** give the corresponding substituted 2-(3-methyloxazolidin-2-ylidene)-*N*-arylthioacetamides **5a–b** and 2-(3,4,4,6-tetramethyloxazan-2-ylidene)-*N*-arylthioacetamide **6** in CH_2Cl_2 in very good isolated yields at 25, −50 and −78 °C. The *N*-arylthioamide function is found exclusively cis to the oxygen and trans to ring nitrogen in **5** and **6**. This assignment was clear from NOESY experiments and X-ray crystal structures (Fig. 1) of compounds **5b** and **6a**. NOSEY experiments on **5a–b** and **6** exhibited cross-peaks between the vinyl proton and protons of the *N*-methyl group, as was previously found with **4a–d**. Protons are spatially near each other.

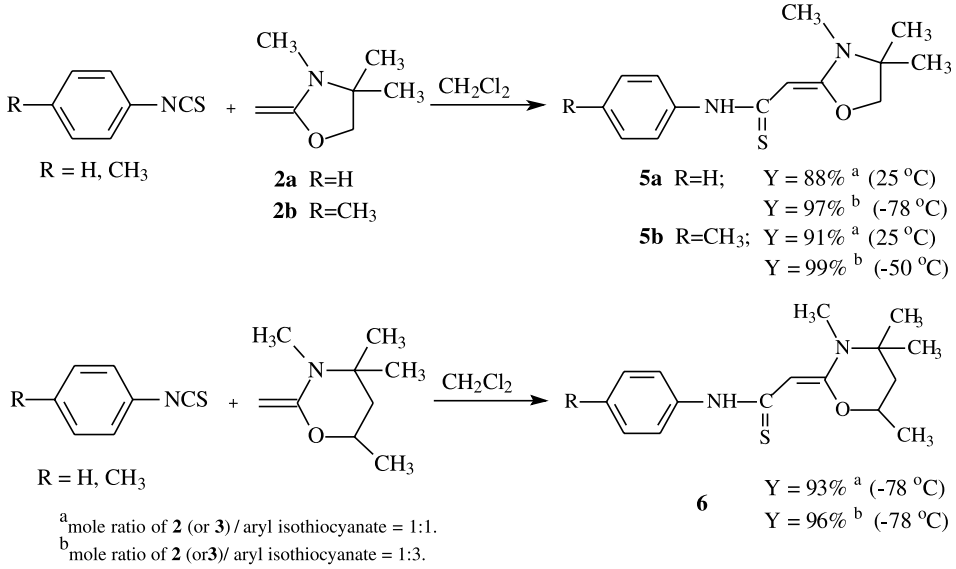
Thioamide adducts **4**, **5** and **6** are not nucleophilic enough to react with a second equivalent of aryl isothiocyanate to give the corresponding 'push–pull' bis-adducts at room temperature. The use of high aryl isothiocyanate to **1**, **2** or **3**



1a R^1=H; R^2=H; R^3=H
1b R^1=H; R^2=H; R^3=CH_3
1c R^1=H; R^2=Et; R^3=H
1d R^1=CH_3; R^2=CH_3; R^3=H
mole ratio of **1** / ArNCS = 1:2

4a R^1=H; R^2=H; R^3=H; Y = 88%
4b R^1=H; R^2=H; R^3=CH_3; Y = 79%
4c R^1=H; R^2=Et; R^3=H Y = 80%
4d R^1=CH_3; R^2=CH_3; R^3=H; Y = 80%

Scheme 3.



[a] mole ratio of **2** (or **3**) / aryl isothiocyanate = 1:1.
[b] mole ratio of **2** (or**3**)/ aryl isothiocyanate = 1:3.

Scheme 4.

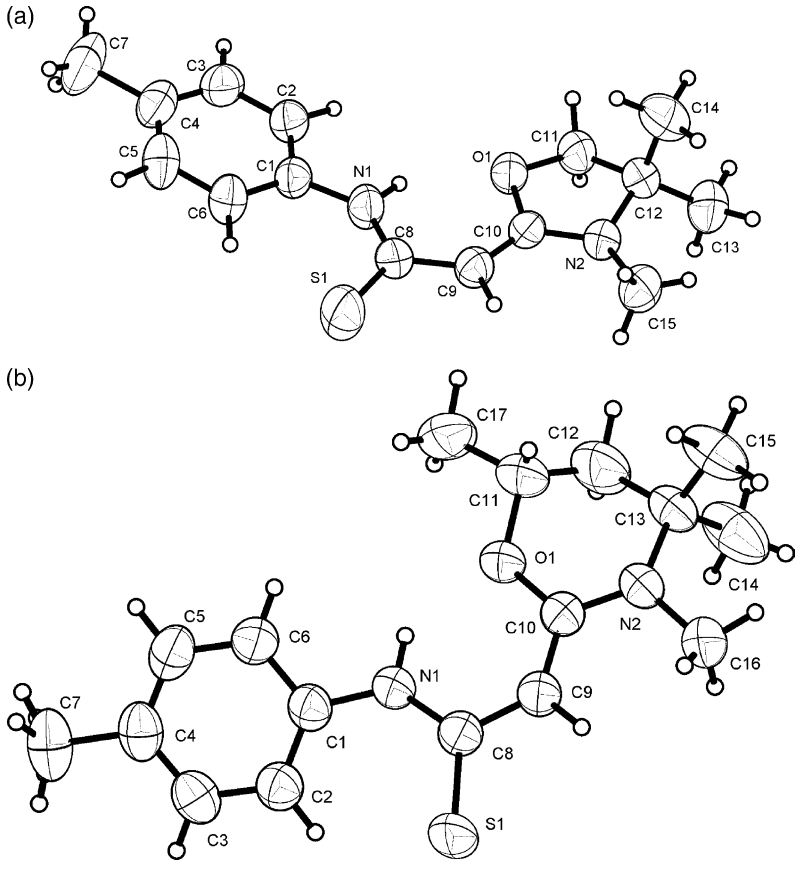
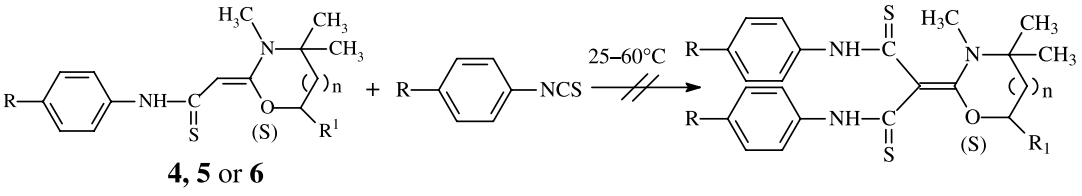
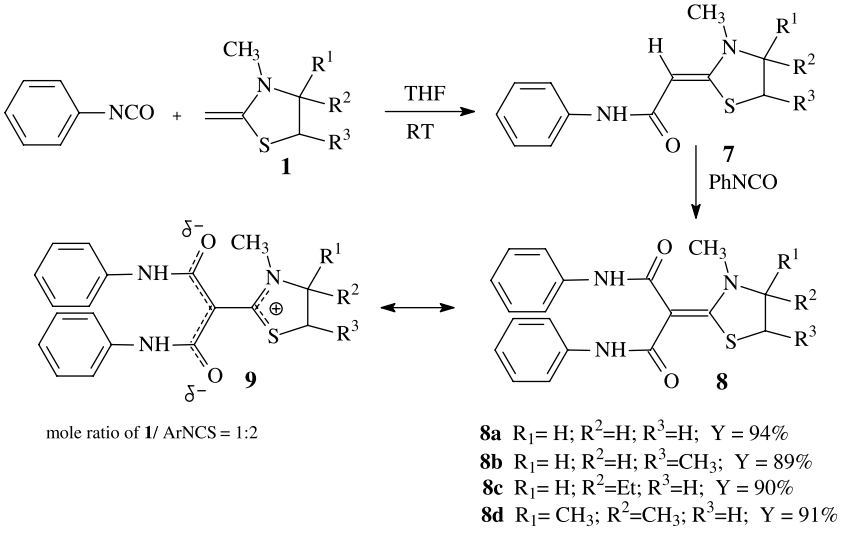


Figure 1. (a) X-ray crystal structure of compound **5b**. (b) X-ray crystal structure of compound **6**.



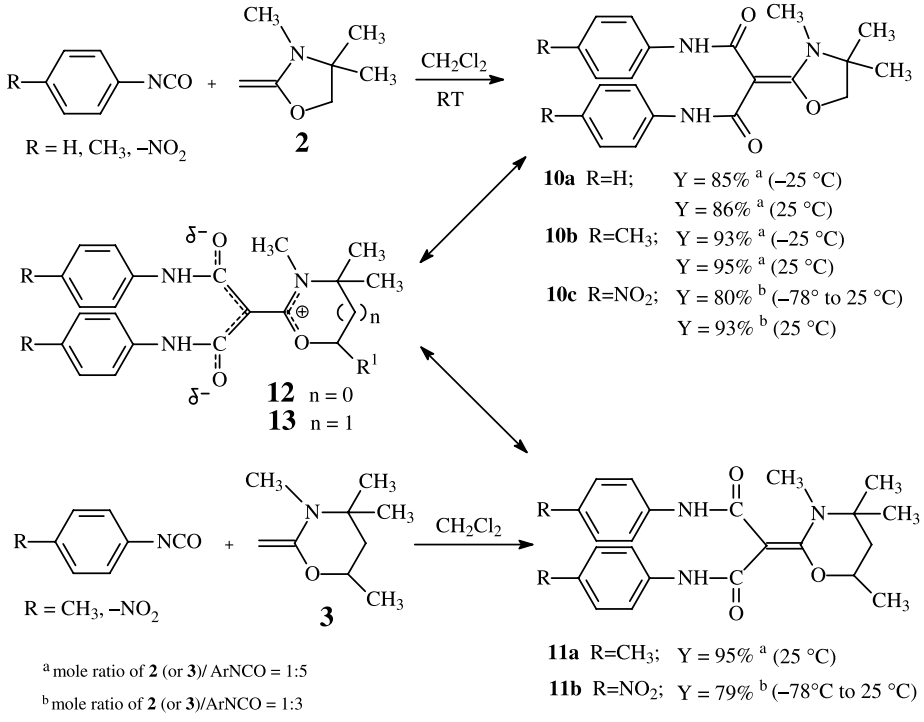
Scheme 5.



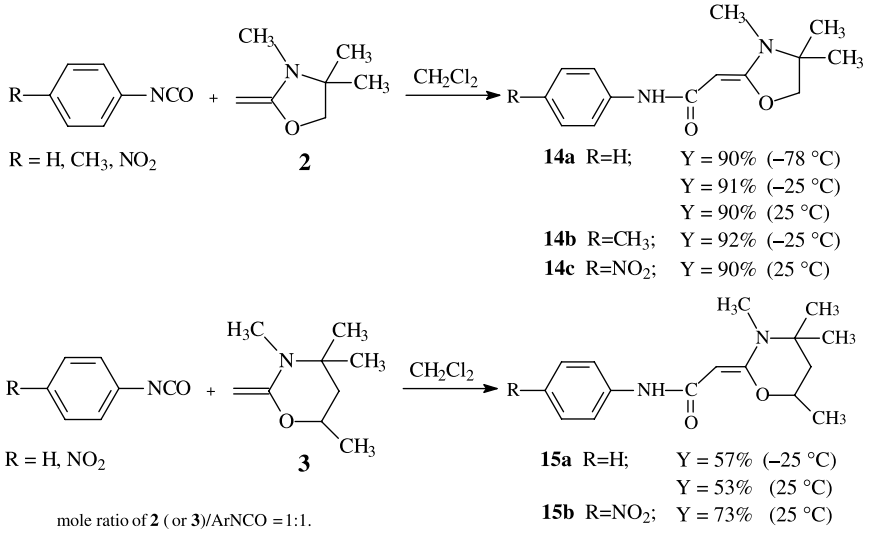
Scheme 6.

mole ratios or raising the temperature to 60 °C did not generate the corresponding bis-adducts (Scheme 5).

Aryl isocyanates are more electrophilic than their corresponding aryl isothiocyanates. Aryl isocyanate reactions with cyclic ketene-*N*,*O* (and *N*,*S*)-acetals **1**, **2**, or **3** did not stop at the monoadduct stage in the presence of excess aryl isocyanate. Thus, the initially formed monoadducts **4**, **5** and **6** add to a second equivalent of aryl isocyanate to afford bis-adducts **8** (Scheme 6), **10** and **11** (Scheme 7), respectively. These reactions all proceed readily in excellent isolated yields in THF or CH_2Cl_2, at, or below, 25 °C. The 'push–pull' bis-amide adducts **8**, **10** and **11** exhibit zwitterionic resonance contributions from hybrid structures **9** (Scheme 6), **12** and **13** (Scheme 7), respectively. The enamine, vinylether and thioether functions provide strong electron donation towards the two amide functions. The charge is localized more on the amide carbonyl oxygens in these zwitterions and β-carbons resemble ordinary vinyl carbons more than they did in the original ketene acetals. This is indicated by the substantial downfield shifts in the ^{13}C NMR spectra experienced by the original α-carbons of **1**, **2** and **3** upon conversion to **8**, **10** and **11**. The β-carbons are also shifted downfield considerably due to substantial charge delocalization to the amide carbonyls. The chemical shifts of the original β-carbons in **1**, **2** and **3** are found at 45–65 ppm. These move downfield to 75–95.5 ppm in **8**, **10** and **11**. Example changes in β-carbon chemical shifts are **8a**: $\Delta\delta=$ 37.9 ppm; **8d**: $\Delta\delta=26.5$ ppm; **10a**: $\Delta\delta=23.1$ ppm; **11a**: $\Delta\delta=22.1$ ppm. The solubilities of **8**, **10** and **11** in hexane



Scheme 7.



Scheme 8.

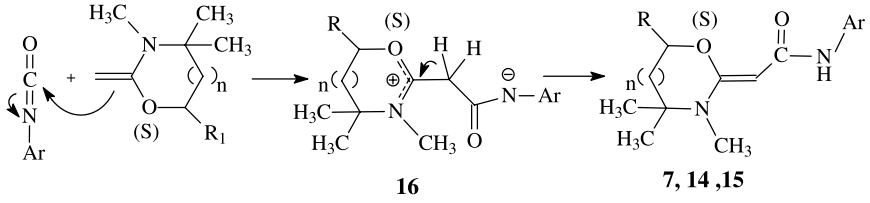
and even ethyl acetate are very low, in accord with the high polarity of these compounds. Hexane is used to precipitate reaction product **8**, **10** and **11**.

When the cyclic ketene acetal/aryl isocyanate ratio was held at 1:1, mono-adducts **14** and **15** were also readily prepared from **2** and **3**, respectively (Scheme 8). Thus, it is clear that bis-adducts **8**, **10**, and **11** are formed by two-step reactions. First, the *N*-methyl cyclic ketene-*N*,X (X=S, O)-acetals **1**, **2**, and **3** rapidly form the monoadduct. Monoadduct formation is much faster than the second aryl isocyanate addition to give the bis-adducts **8**, **10** and **11**.

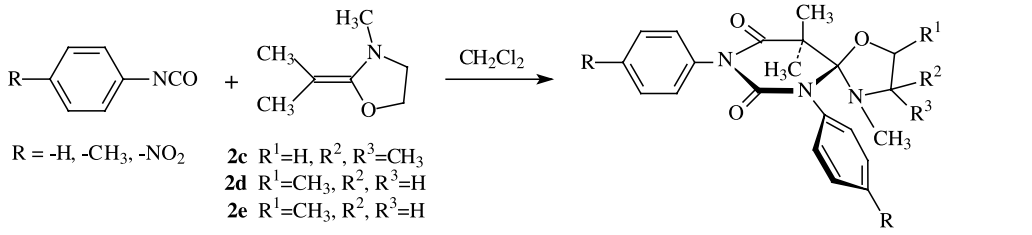
Monoadduct formation occurs as shown in Scheme 10. Nucleophilic attack by the acetal's β-carbon on the isocyanate (or isothiocyanate) function's carbon generates the zwitterionic intermediate **16**, which now features an acidic proton adjacent to the ring. Loss of this acidic proton and proton capture by the amide nitrogen regenerates the cyclic ketene-*N*,X-acetal function in the product (Scheme 9).

N-Methyl cyclic ketene-*N*,*O*-acetals **2** and **3**, which contain two methyl groups at the β-carbon atom of the acetal double bond, behaved differently. When examples of **2** and **3**, which contain two β-methyls, were reacted with aryl isocyanate in CH_2Cl_2 at room temperature or −25 °C, instead of giving bis-adducts, the reactions produced the spirobicyclic 6/5 and 6/6 ring systems **17** and **18** (Scheme 10). In sharp contrast, *N*-methyl cyclic ketene-*N*,*S*-acetals containing two methyl groups on the β-carbon did not afford spirobicyclic rings systems when reacted with aryl isocyanates. Instead, many spots were observed on TLC plates. No major product was formed or isolated and these reactions were not further investigated.

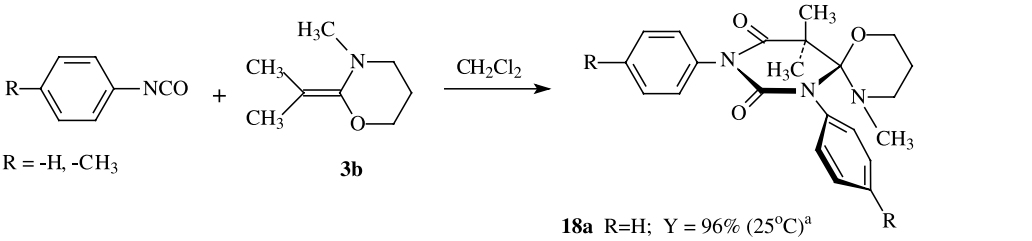
The 6/5 spirobicyclic products, **17c**, **17d** and **17f**, each have two diastereomers, because each contains two carbons (C-3



Scheme 9.



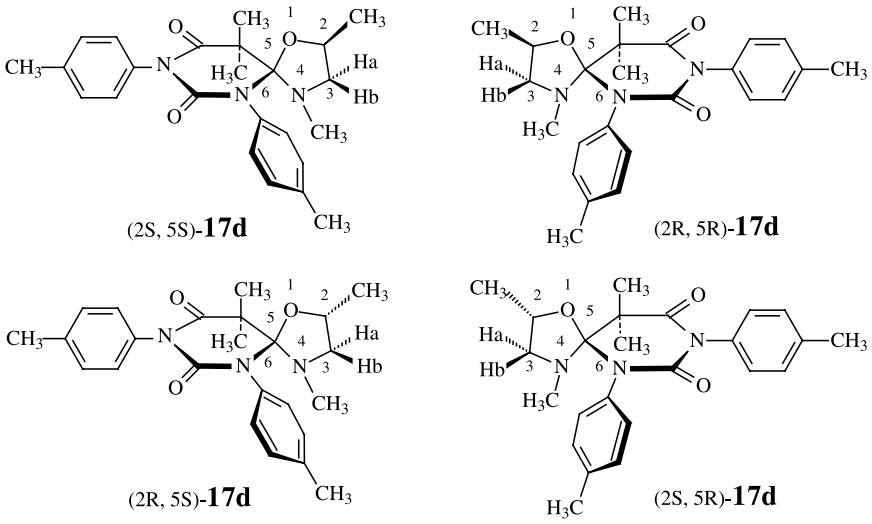
17a R=H; R^1=H, R^2, R^3=CH_3; Y = 94% (–25 °C)[a]
Y = 98% (25 °C)[a]
17b R=CH_3; R^1=H, R^2, R^3=CH_3; Y = 91% (–25 °C)[a]
Y = 92% (25 °C)[a]
17c R= H; R^1=CH_3, R^2, R^3=H; Y = 92% (–25 °C)[a]
Y = 94% (25 °C)[a]
17d R=CH_3; R^1=CH_3, R^2, R^3=H; Y = 95% (–25 °C)[a]
Y = 97% (25 °C)[a]
17e R=NO_2; R^1=H, R^2, R^3=CH_3; Y = 92% (–20 °C)[b]
Y = 95% (25 °C)[b]
17f R=NO_2; R^1=CH_3, R^2, R^3=H; Y = 91% (–20 °C)[b]
Y = 93% (25 °C)[b]



18a R=H; Y = 96% (25°C)[a]
18b R=CH_3; Y = 93% (-25°C)[a]
Y = 97% (25°C)[a]

[a] mole ratio of **2** (or **3**)/ ArNCO = 1:5
[b] mole ratio of **2** (or **3**)/ArNCO = 1:3.

Scheme 10.



Scheme 11.

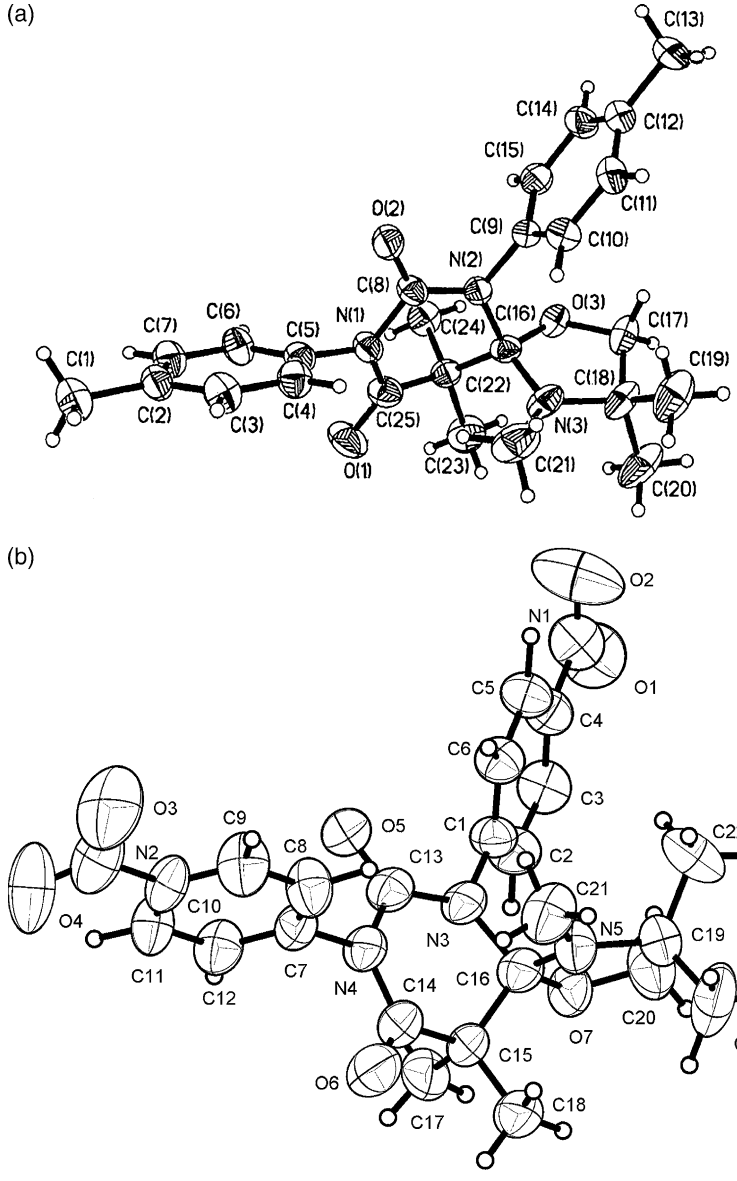
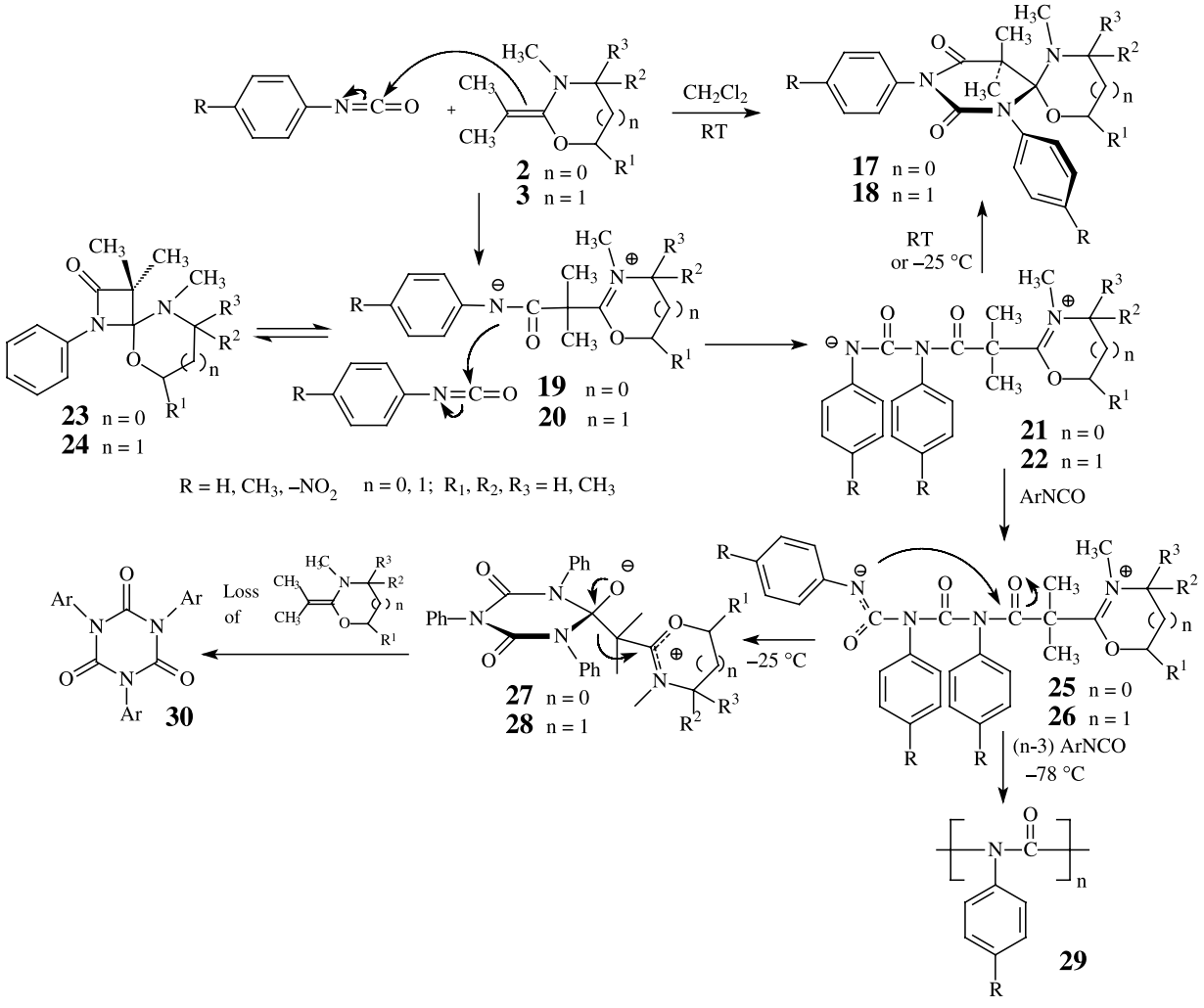


Figure 2. (a) X-ray crystal structure of compound **17b**. (b) X-ray crystal structure of compound **17e**.

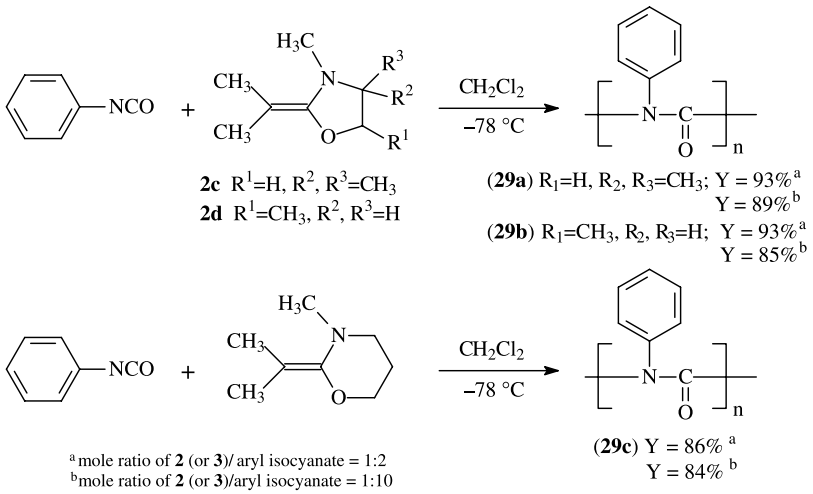
and C-5) whose configurations can be *R* or *S*. The ^{1}H and ^{13}C NMR spectra of each of these three diastereomer mixtures, prior to separation by flash chromatography over silica gel, clearly exhibited two sets of peaks corresponding to each diastereomer. The mole ratio of two diasteromers is nearly 1:1 for all three cases. Integration of the methyl peaks from ^{1}H NMR spectroscopy (protons from R^1, R^2, R^3) versus the aromatic protons demonstrated that **17/18** contained two molecules of ArNCO.

The diastereomers of **17d** are used here as the example pair to illustrate how stereochemistry was assigned by use of their NMR spectra. Scheme 11 shows the structures of the diastereomers of **17d**. These diastereomers exist as two racemic sets of enantiomers (e.g., (2*S*,5*S*)-**17d** and (2*R*,5*R*)-**17d** along with (2*R*,5*S*)-**17d** and (2*S*,5*R*)-**17d**. These two diastereomers were easily separated by flash chromatography. The configuration at C-2 was decided by proton chemical shift of the methyl group bound to C-2. These methyl resonances were observed at 1.11 and 0.46 ppm. The upfield doublet at 0.46 ppm belongs to the C-2 methyl of the 2*S*,5*S*-**17d** and 2*R*,5*R*-**17d** enantiomer pair, because this methyl group lies in the face of this phenyl ring on N-6. Therefore, it experiences a strong upfield shift. In contrast, the methyl protons of the 2*R*,5*S*-**17d** and 2*S*,5*R*-**17d** enantiomer pair lie outside this shielding zone. Therefore, this C-2 methyl doublet's chemical shift is assigned to the at 1.12 ppm resonance. The proton bound to C-2 in each diastereomer also fit this pattern. Thus, the proton chemical shifts on C-2 for (2*S*,5*S*)-**17d** and (2*R*,5*R*)-**17d** is a multiplet at 4.11 ppm. However, the C-2 proton in 2*R*,5*S*-**17d** and 2*S*,5*R*-**17d** is found substantially upfield at 3.35 ppm, because it lies within the shielding anisotropy region of the aryl ring at N-6. X-ray crystal structures of **17b** and **17e** in Figure 2, provide further support to these assignments. Both crystal structures demonstrate that the plane of the phenyl ring at N-6 is approximately perpendicular to central ring in these compounds. Models show this conformation is also favored in solution, because the spiroheterocyclic five-membered ring interferes sterically with the *ortho*-hydrogen on the N-6 aryl ring.

The mechanism for spirobicyclic ring formation is shown in Scheme 12. Reaction of **2** or **3** (two β-methyls) with the first aryl isocyanate affords the zwitterions **19/20**. These zwitterions cannot undergo transfer of an acidic proton to nitrogen to form monoadducts as was the case during the formation of **4**, **5**, **6**, **7**, **14** and **15** (e.g., Schemes 3, 4, 6, 7 and 8). However **19** or **20** could reversibly cyclize to form spirobicyclic lactams, **23** or **24**. However, these lactams were not observed or isolated.



Scheme 12.

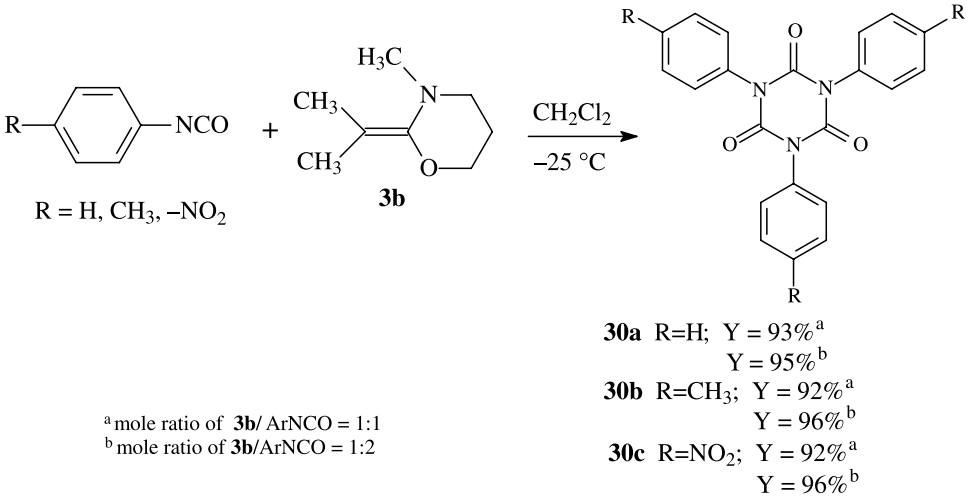


Scheme 13.

Instead, a second equivalent of aryl isocyanate reacts by nucleophilic attack of **19/20** on the isocyanate carbon to form zwitterion **21/22**. Cyclization of **21/22** then occurs to form the stable spiro-six-membered ring in **17/18** at temperatures between −25 and 25 °C. Cyclization to **17/18** occurs more rapidly than another nucleophilic addition of the negatively charged amide nitrogen of **21**, **22** to a third equivalent of aryl isocyanate to form the zwitterions **25/26**. Thus, the spirobicyclic 6/5 and 6/6 ring products, **17** and **18**, were obtained. X-ray crystal structures of **17b** and **17d** confirmed the formation spirobicyclic structures (Fig. 2). These structures also fit the detailed NMR analyses described earlier.

The reaction pathways change when cyclic ketene-*N*,*O*-acetals with two methyl groups at the β-carbon are reacted at −78 °C. At this low temperature, these *N*,*O*-acetals, **2** and **3** do not form the spirobicyclic 6/5 and 6/6 ring products upon reacting with isocyanates. Instead of cyclizing to **17/18**, zwitterions **21/22** (shown in Scheme 12) continue to react with additional phenyl isocyanate to generate poly(phenylisocyanate) **29** (Scheme 13). Molecular weights of 2000–4000 were observed when substantial or stoichiometric amounts of **2** (R=CH_3) were employed, indicating that this polymerization is very fast relative to the initial addition of **2** to phenylisocyanate. Adding only trace amounts of **2** to phenylisocyanate gives higher molecular weight polymers.

Curiously, the six-membered ring cyclic ketene-*N*,*O*-acetal **3b** does not generate poly(aryl isocyanates) when reacted with aryl isocyanates at −25 °C in CH_2Cl_2. Instead 1,3,5-triaryl-[1,3,5]triazinan-2,4,6-triones **30** were produced (Scheme 14). While **3b** acts as an anionic polymer initiator at −78 °C, **3b** leads to **30** at −25 °C because each of the cyclizations of zwitterions **26** (R=H, CH_3, NO_2) occur faster then the addition of **26** to a fourth aryl isocyanate. Cyclization of **26** gives intermediates **28** (Scheme 12), which eliminate the original cyclic ketene-*N*,*O*-acetal **3b** to form 1,3,5-triaryl-[1,3,5]triazinane-2,4,6-triones **30a–c**. The structures of **30a–c** were established by NMR and IR spectroscopy



Scheme 14.

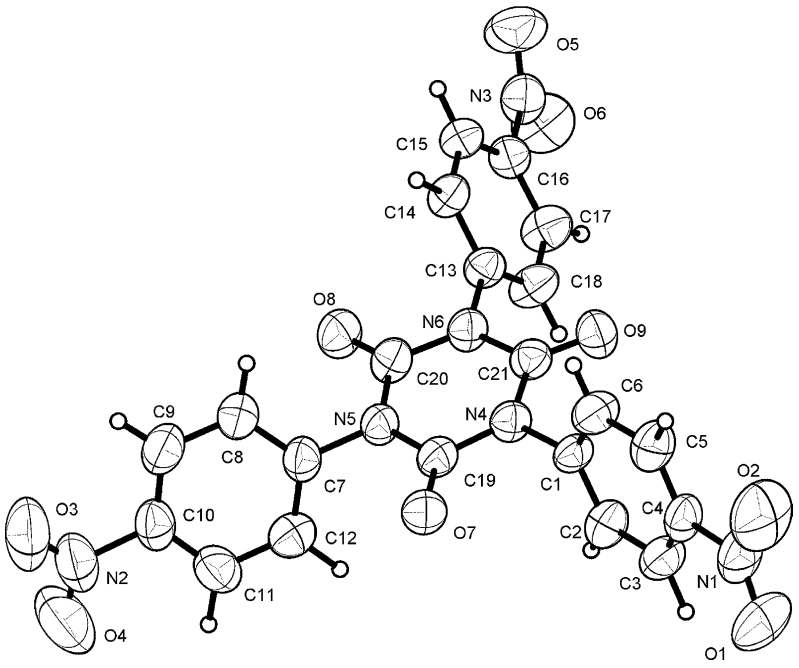


Figure 3. X-ray crystal structure of compound **30c**.

and melting points. Furthermore, the crystal structure was obtained for **30c** (Fig. 3).

3. Conclusions

The nucleophilic character of the exocyclic β-carbon of cyclic ketene-*N*,X (X=O, S)-acetals was established and demonstrated in nucleophilic reactions with aryl isocyanates, and aryl isothiocyanates, at different temperatures. Mono-α,β-unsaturated thioamides and both mono- and bis-α,β-unsaturated amide electronic 'push–pull' products were obtained when the β-carbon of the cyclic ketene acetal contained two hydrogens. However, when no hydrogens were present at the β-carbon, spirobicyclic six/five and six/six-membered ring systems were formed in reactions of cyclic ketene-*N*,*O*-acetals with aryl isocyanates at 25−−25 °C. At −78 °C, however, both five- and six-membered ring *N*,*O*-acetals initiated aryl isocyanate polymerizations. A third reaction pathway was also observed, six-membered ring *N*,*O*-acetal **3a** generated 1,3,5-triaryl-[1,3,5]triazinane-2,4,6-triones when reacted with aryl isocyanates. All these reactions proceed under mild conditions to give excellent isolated yields in most cases.

4. Experimental

4.1. General methods

Melting points were recorded with a Mel-Temp apparatus and were uncorrected (using a heating rate of 2 °C/min near the mp). The IR spectra were recorded on FT infrared spectrometer as films on KBr plates. The ^{1}H and ^{13}C NMR spectra were recorded using 300 MHz spectrometer operating at 300 MHz for proton and 75 MHz for carbon. Chemical shifts were reported in ppm downfield from Me_4Si used as the internal standard. Splitting patterns are designated as 's, d, t, q, and m'; these symbols indicate 'singlet, doublet, triplet, quartet, and multiplet', respectively. All reactions were carried out under a dried nitrogen atmosphere. Acetonitrile and triethylamine were distilled from calcium hydride under nitrogen. Dichloromethane and nitromethane were pre-dried with $CaCl_2$ and then distilled from calcium hydride under nitrogen. Tetrahydrofuran (THF) was distilled from Na metal/benzophenone ketyl. All other commercially obtained reagents were used as received. The silica gel used for the column chromatography was purchased from Aldrich Company (70–230 mesh).

4.1.1. (2*Z*)-(3-Methylthiazolidin-2-ylidene)-*N*-phenylthioacetamide (4a). The *N*-methyl cyclic ketene-*N*,*S*-acetal (3-methyl-2-methylenethiazolidine) (0.23 g, 2.0 mmol) was directly added into THF (40 mL). While stirring, phenyl isothiocyanate (0.54 g, 4.0 mmol) was added to this THF solution under nitrogen at room temperature. An immediate exothermic reaction occurred. The reaction mixture was stirred at room temperature under nitrogen for 3 h and then poured into *n*-hexane (100 mL) to precipitate the product. 2-(3-Methyl-thiazolidin-2-ylidene)-*N*-phenylthioacetamide **4a** was obtained in an isolated yield of 88% (0.45 g). The same procedure was used for compounds **4b–d**, **5a–b**, **6**, **14** and **15**.

Mp 157–159 °C. ^{1}H NMR (300 MHz, DMSO): δ 10.30 (s, 1H), 7.67–7.07 (m, 5H), 5.95 (s, 1H), 3.59 (t, J=7.8 Hz, 2H), 2.80 (t, J=7.8 Hz, 2H), 2.90 (s, 3H). ^{13}C NMR (DMSO): δ 188.0, 166.1, 140.7, 128.1, 123.7, 122.6, 95.5, 55.3, 35.3, 28.2. IR (neat): 3400–3300, 2932, 2857, 1587, 1515, 1452, 1351, 1195, 738 cm^{-1}.

4.1.2. (2*Z*)-(3,5-Dimethylthiazolidin-2-ylidene)-*N*-phenylthioacetamide (4b). Mp 158–160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.37 (s, 1H), 7.33–7.13 (m, 5H), 5.83 (s, 1H), 3.59 (dd, J=7.2, 10.2 Hz, 1H), 3.59 (m, 1H), 3.26 (dd, J=7.2, 10.2 Hz, 1H), 2.81 (s, 3H), 1.38 (d, 3H). ^{13}C NMR ($CDCl_3$): δ 188.5, 168.8, 139.2, 128.8, 125.3,

124.2, 92.4, 62.8, 38.9, 35.4, 19.2. IR (neat): 3400–3300, 2962, 2924, 1595, 1530, 1495, 1301, 1230, 1183, 911, 750, 697 cm^{-1}. Anal. Calcd for $C_{13}H_{16}N_2S_2$: C, 59.08; H, 6.05; N, 10.60; S 24.26. Found: C, 59.23; H, 5.93; N, 10.77; S, 23.92.

4.1.3. (2*Z*)-(4-Ethyl-3-methylthiazolidin-2-ylidene)-*N*-phenylthioacetamide (4c). Mp 162–164 °C. ^1H NMR (300 MHz, acetone-d_6): δ 9.45 (s, 1H), 7.70–7.07 (m, 5H), 5.93 (s, 1H), 3.81 (m, 1H), 3.12 (dd, $J=7.8$, 11.1 Hz, 1H), 2.90 (s, 3H), 2.80 (dd, $J=3.6$, 11.1 Hz, 1H), 1.72–1.56 (m, 2H), 0.91 (t, $J=7.5$ Hz, 3H). ^{13}C NMR (acetone-d_6): δ 190.5, 167.3, 142.1, 129.3, 125.0, 124.0, 96.0, 68.4, 34.8, 33.1, 24.4, 10.1. IR (neat): 3400–3300, 2964, 1595, 1524, 1494, 1299, 1231, 1191, 756, 695 cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_2S_2$: C, 60.43%; H, 6.47; N, 10.06; S, 23.04. Found: C, 60.24; H, 6.64; N, 9.88; S, 23.43.

4.1.4. (2*Z*)-(3,4,4-Trimethylthiazolidin-2-ylidene)-*N*-phenylthioacetamide (4d). Mp 164–166 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.35–7.15 (m, 5H), 5.82 (s, 1H), 2.90 (s, 2H), 2.66 (s, 3H), 1.31 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 188.5, 168.2, 139.2, 128.8, 125.3, 124.3, 93.1, 66.2, 41.9, 30.80, 23.9. IR (neat): 3400–3300, 2970, 1590, 1520, 1494, 1297, 1236, 1183, 910, 757, 715 cm^{-1}. Anal. Calcd for $C_{14}H_{18}N_2S_2$: C, 60.43; H, 6.47; N, 10.06; S, 23.04. Found: C, 60.26; H, 6.67; N, 10.25; S, 22.76.

4.1.5. (2*Z*)-(3,4,4-Trimethyloxazolidin-2-ylidene)-*N*-phenylthioacetamide (5a). Mp 136–137 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.14 (s, 1H), 7.61–7.11 (m, 5H), 5.11 (s, 1H), 4.21 (s, 2H), 2.69 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 190.3, 166.1, 140.1, 128.3, 125.2, 124.5, 82.6, 79.0, 60.3, 26.5, 22.8. IR (neat): 3376, 2976, 1588, 1507, 1433, 1343, 1147, 936, 764, 699 cm^{-1}.

4.1.6. *N*-*p*-Tolyl-(2*Z*)-(3,4,4-trimethyloxazolidin-2-ylidene)-thioacetamide (5b). Mp 153–154 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 9.37 (s, 1H), 7.44–7.14 (m, 4H), 5.12 (s, 1H), 4.23 (s, 2H), 2.71 (s, 3H), 2.33 (s, 3H), 1.31 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.6, 162.2, 137.5, 135.2, 129.1, 124.9, 83.2, 79.0, 60.3, 26.6, 22.9, 22.0. IR (neat): 3378, 2971, 2927, 1583, 1522, 1438, 1338, 1260, 1137, 925, 748, 697 cm^{-1}.

4.1.7. 2-(3,4,4,6-Tetramethyl-[1,3]oxazinan-2-ylidene)-*N*-*p*-tolylthioacetamide (6). Mp 170–172 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 9.85 (s, 1H), 7.52–7.14 (m, 4H), 5.20 (s, 1H), 4.43 (m, 1H), 2.80 (s, 3H), 1.97–1.79 (m, 2H), 1.46 (d, $J=6.2$ Hz, 3H), 1.34 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 190.4, 156.5, 138.0, 134.7, 129.0, 124.1, 88.7, 69.6, 55.0, 44.9, 32.1, 27.8, 26.6, 21.0, 20.4. IR (neat): 3348, 2968, 2924, 2360, 1594, 1537, 1442, 1256, 1137, 1309, 1142, 1120, 985 cm^{-1}.

4.1.8. Preparation of 2-(3-methylthiazolidin-2-ylidene)-*N*,*N*′-diphenylmalonamide (8a). The *N*-methyl cyclic ketene-*N*,*S*-acetal (3-methyl-2-methylenethiazolidine) (0.23 g, 2.0 mmol) was directly added into THF (60 mL). Phenyl isocyanate (0.48 g, 4.00 mmol) was added to this solution while stirring under nitrogen at room temperature. An immediate exothermic reaction occurred. The reaction mixture was stirred at room temperature under nitrogen for 3 h and then poured into *n*-hexane (100 mL) to precipitate the product. 2-(3-Methyl-thiazolidin-2-ylidene)-*N*,*N*′-diphenylmalonamide **8a** was obtained in an isolated yield of 94% (0.67 g). The same procedure was used for compounds **8b–d**, **10a–c**, **11a–b**, **17**, **18**, **29** and **30**.

Mp 188–190 °C. ^1H NMR (300 MHz, DMSO): δ 9.37 (s, 2H), 7.61–6.88 (m, 10H), 3.49 (t, $J=6.9$ Hz, 2H), 2.90 (s, 3H), 2.80 (t, $J=7.8$ Hz, 2H). ^{13}C NMR (DMSO): δ 168.0, 166.1, 140.7, 128.1, 123.7, 122.6, 95.5, 55.3, 35.3, 28.2. IR (KBr): 3400–3200, 2932, 2857, 1587, 1515, 1452, 1351, 1195, 738 cm^{-1}. Anal. Calcd for $C_{19}H_{19}N_3O_2S$: C, 64.61; H, 5.38; N, 11.89; O, 9.06; S, 9.06. Found: C, 64.73; H, 5.27; N, 11.71; S, 8.93.

4.1.9. 2-(3,5-Dimethylthiazolidinylidene)-*N*,*N*′-diphenylmalonamide (8b). Mp 190–192 °C. ^1H NMR (300 MHz, DMSO): δ 10.02 (s, 2H), 7.62–7.00 (m, 10H), 3.90 (m, 1H), 3.50 (m, 1H), 3.44 (m, 1H), 2.95 (s, 3H), 1.30 (d, $J=6.0$ Hz, 3H). ^{13}C NMR (DMSO): δ 167.6, 165.6, 139.1, 128.6, 122.7, 119.2, 92.6, 63.6, 38.6, 35.5, 19.7. IR (KBr): 3400–3200, 2937, 2849, 1583, 1521, 1447, 1355, 1198, 741 cm^{-1}. Anal. Calcd for $C_{20}H_{21}N_3O_2S$: C, 65.41; H, 5.72; N, 11.44; O, 8.71; S, 8.71. Found: C, 65.10; H, 5.91; N, 11.33; S, 8.78.

4.1.10. 2-(4-Ethyl-3-methylthiazolidin-2-ylidene)-*N*,*N*′-diphenylmalonamide (8c). Mp 194–196 °C. ^1H NMR (300 MHz, DMSO): δ 9.88 (s, 2H), 7.61–6.99 (m, 10H), 3.82 (m, 1H), 3.18 (dd, $J=8.1$, 10.8 Hz, 1H), 2.95 (s, 3H), 2.77 (dd, $J=4.8$, 10.8 Hz, 1H), 1.85–1.60 (m, 2H), 0.89 (t, $J=6.9$ Hz, 3H). ^{13}C NMR (DMSO): δ 168.3, 165.8, 139.2, 128.6, 122.7, 119.0, 93.0, 69.9, 39.9, 30.4, 25.1, 9.8. IR (KBr): 3400–3200, 2967, 1643, 1589, 1521, 1436, 1309, 1243, 905, 749, 693 cm^{-1}. Anal. Calcd for $C_{21}H_{23}N_3O_2S$: C, 66.16; H, 6.03; N, 11.02%; O, 8.39; S, 8.39. Found: C, 66.40; H, 6.01; N, 10.73; S, 8.56.

4.1.11. *N*,*N*′-Diphenyl-2-(3,4,4-trimethylthiazolidin-2-ylidene)-malonamide (8d). Mp 197–199 °C. ^1H NMR (300 MHz, DMSO): δ 9.85 (s, 2H), 7.61–7.01 (m, 10H), 3.00 (s, 2H), 2.80 (s, 3H), 1.33 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 168.9, 165.9, 139.2, 128.6, 122.6, 119.1, 91.7, 67.8, 40.2, 34.30, 23.6. IR (KBr): 3400–3200, 2970, 1590, 1520, 1494, 1297, 1236, 1183, 910, 757, 715 cm^{-1}. Anal. Calcd for $C_{21}H_{23}N_3O_2S$: C, 66.16; H, 6.03; N, 11.02; O, 8.39; S, 8.39. Found: C, 65.88; H, 6.34; N, 10.84; S, 8.13.

4.1.12. *N*,*N*′-Diphenyl-2-(3,4,4-trimethyloxazolidin-2-ylidene)-malonamide (10a). Mp 161–162 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.99 (s, 2H), 7.56–7.03 (m, 10H), 4.25 (s, 2H), 2.95 (s, 3H), 1.44 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 169.7, 167.0, 140.7, 130.1, 124.4, 121.9, 82.1, 78.5, 63.6, 32.4, 25.0. IR (KBr): 3330, 3020, 2960, 1640, 1595, 1540, 1440, 1320, 1250, 1055, 960, 760 cm^{-1}. Anal. Calcd for $C_{21}H_{23}O_3N_3$: C, 69.05; H, 6.30; N, 11.27. Found: C, 68.86; H, 6.54; N, 11.27.

4.1.13. *N*,*N*′-Di-*p*-tolyl-2-(3,4,4-trimethyloxazolidin-2-ylidene)-malonamide (10b). Mp 168–170 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.92 (s, 2H), 7.42–7.09 (m, aromatic H, 8H), 4.21 (s, 2H), 2.93 (s, 3H), 2.29 (s, 6H), 1.40 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 167.8, 165.6, 136.5, 129.2, 120.7, 79.4, 62.1, 60.3, 31.0, 23.6, 20.8. IR (KBr): 3427, 3027,

1660, 1625, 1521, 1437, 1326, 1242, 1065, 814, 786 cm^{-1}. Anal. Calcd for $C_{23}H_{27}N_3O_3$: C, 70.24; H, 6.87; N, 10.69. Found: C, 70.03; H, 7.06; N, 10.62.

4.1.14. *N*,*N*′-Bis-(4-nitrophenyl)-2-(3,4,4-trimethyloxazolidin-2-ylidene)-malonamide (10c). Mp 195–196 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 10.58 (s, 2H), 8.19–7.87 (m, 8H), 4.66 (s, 2H), 3.08 (s, 3H), 1.54 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 169.8, 166.6, 149.7, 147.4, 125.6, 119.4, 78.7, 78.5, 64.5, 30.2, 23.6. IR (KBr): 3581, 3238, 2968, 1697, 1625, 1575, 1507, 1335, 1257, 1118, 1056, 867, 761 cm^{-1}.

4.1.15. *N*,*N*′-Bis-(4-tolyl)-2-(3,4,4,6-tetramethyl-[1,3]-oxazinan-2-ylidene)-malonamide (11a). Mp 166–168 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 10.03 (s, 2H), 7.40–7.08 (m, 8H), 4.57–4.45 (m, 1H), 3.11 (s, 3H), 2.29 (s, 6H), 2.04–1.91 (m, 2H), 1.55 (d, J=5.2 Hz, 3H), 1.48 (s, 3H), 1.47 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 169.6, 166.3, 137.0, 132.1, 129.2, 120.3, 88.5, 70.9, 57.7, 45.1, 35.5, 27.5, 27.2, 20.7, 20.0. IR (KBr): 3435, 2927, 1638, 1507, 1313, 1245, 1052, 821, 728, 505 cm^{-1}.

4.1.16. *N*,*N*′-Bis-(4-nitrophenyl)-2-(3,4,4,6-tetramethyl-[1,3]oxazinan-2-ylidene)-malonamide (11b). Mp 205–208 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 10.64 (s, 2H), 8.16–7.66 (m, 8H), 4.73 (m, 1H), 3.21 (s, 3H), 2.15–2.02 (m, 2H), 1.65 (d, J=5.2 Hz, 3H), 1.56 (s, 3H), 1.55 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 170.7, 165.9, 147.4, 145.8, 142.1, 129.9, 125.1, 124.8, 119.7, 118.8, 82.7, 72.3, 58.8, 44.4, 36.1, 27.5, 27.0, 20.3. IR (KBr): 3412, 3074, 2990, 1720, 1650, 1600, 1536, 1491, 1407, 1335, 1257, 1118, 1056, 846, 744 cm^{-1}.

4.1.17. *N*-Phenyl-2-(3,4,4-trimethyloxazolidin-2-ylidene)-acetamide (14a). Mp 151–152 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.26 (s, 1H), 7.55–6.99 (m, 4H), 4.18 (s, 2H), 4.03 (s, 1H), 2.63 (s, 3H), 1.27 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 166.0, 161.7, 139.6, 128.6, 122.3, 119.5, 78.6, 70.4, 60.0, 26.5, 22.5. IR (KBr): 3289, 2964, 1757, 1532, 1255, 1038, 831, 743, 521 cm^{-1}. Anal. Calcd for $C_{14}H_{18}O_2N_2$: C, 68.31; H, 7.31; N, 11.38. Found: C, 68.48; H, 7.11; N, 11.24.

4.1.18. *N*-*p*-Tolyl-2-(3,4,4-trimethyloxazolidin-2-ylidene)-acetamide (14b). Mp 160–162 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.42–7.07 (m, 4H), 4.17 (s, 2H), 4.02 (s, 1H), 2.62 (s, 3H), 2.29 (s, 3H), 1.26 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 166.0, 161.6, 137.0, 131.8, 129.1, 119.7, 78.5, 70.4, 60.0, 26.6, 22.5, 20.7. IR (KBr): 3295, 2976, 1760, 1523, 1253, 1041, 821, 731, 510 cm^{-1}. Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.24; H, 7.69; N, 10.77. Found: C, 69.10; H, 7.93; N, 10.53.

4.1.19. *N*-*p*-Nitrophenyl-2-(3,4,4-trimethyloxazolidin-2-ylidene)-acetamide (14c). Mp 190–193 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.16–7.70 (m, 4H), 4.24 (s, 2H), 4.07 (s, 1H), 2.68 (s, 3H), 1.32 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 168.9, 162.4, 146.2, 142.2, 125.1, 118.3, 80.4, 70.3, 56.1, 26.7, 22.8. IR (neat): 3567, 3198, 2982, 1709, 1633, 1537, 1515, 1324, 1237, 1131, 1061, 911, 864, 757 cm^{-1}.

4.1.20. *N*-Phenyl-2-(3,4,4,6-tetramethyl-[1,3]oxazinan-2-ylidene)-acetamide (15a). Mp 164–166 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 8.82 (s, 1H), 7.54–6.95 (m, 5H), 4.42 (m, 1H), 4.10 (s, 1H), 2.70 (s, 3H), 1.90–1.70 (m, 2H), 1.51 (d, J=6.2 Hz, 3H), 1.32 (s, 3H), 1.25 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 161.3, 154.3, 128.7, 125.4, 118.7, 119.1, 71.3, 67.6, 55.4, 46.7, 28.6, 26.9, 22.4, 17.2.

4.1.21. *N*-*p*-Nitrophenyl-2-(3,4,4,6-tetramethyl-[1,3]-oxazinan-2-ylidene)-acetamide (15b). Mp 194–196 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.16–7.62 (m, 4H), 4.45 (m, 1H), 4.12 (s, 1H), 2.74 (s, 3H), 1.99–1.82 (m, 2H), 1.56 (d, J=6.2 Hz, 3H), 1.35 (s, 3H), 1.32 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 165.0, 157.5, 132.5, 125.2, 119.6, 117.9, 72.5, 69.7, 55.6, 47.5, 30.5, 27.8, 26.7, 20.6. IR (neat): 3587, 3191, 2974, 1703, 1625, 1538, 1502, 1335, 1257, 1112, 1056, 861, 761 cm^{-1}.

4.1.22. 3,3,4,10,10-Pentamethyl-6,8-diphenyl-1-oxa-4,6,8-triazaspiro[4,5]decane-7,9-dione (17a). Mp 147–148 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.16–7.44 (m, 10H), 3.49 (d, J=6.8 Hz, 1H), 2.67 (d, J=6.8 Hz, 1H), 2.64 (s, 3H), 1.71 (s, 3H), 1.33 (s, 3H), 1.06 (s, 3H), 0.78 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 174.7, 152.4, 136.2, 135.8, 131.4, 131.3, 131.1, 128.9, 128.4, 127.9, 108.2, 77.7, 59.3, 48.1, 26.3, 26.1, 24.7, 24.6, 19.0. IR (KBr): 2980, 2940, 1710, 1660, 1595, 1490, 1390, 1315, 1180, 1081, 840, 690 cm^{-1}. Anal. Calcd for $C_{23}H_{27}O_3N_3$: C, 70.24; H, 6.87; N, 10.69. Found: C, 70.01; H, 7.24; N, 10.39.

4.1.23. 3,3,4,10,10-Pentamethyl-6,8-di-*p*-tolyl-1-oxa-4,6,8-triazaspiro[4,5]decane-7,9-dione (17b). Mp 165–167 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.26–7.03 (m, 10H), 3.48 (d, J=7.7 Hz, 1H), 2.71 (d, J=7.7 Hz, 1H), 2.61 (s, 3H), 2.35 (s, 6H), 1.68 (s, 3H), 1.32 (s, 3H), 1.06 (s, 3H), 0.8 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 174.7, 152.5, 137.8, 133.5, 131.1, 130.7, 129.5, 129.3, 128.7, 128, 108.1, 77.6, 59.2, 48.1, 26.3, 26.2, 24.8, 24.7, 21.1, 19.0. IR (KBr): 2985, 1735, 1678, 1507, 1393, 1327, 1189, 1034, 821, 723, 519 cm^{-1}. Anal. Calcd for $C_{25}H_{31}N_3O_3$: C, 71.27; H, 7.36; N, 9.98. Found: C, 71.04; H, 7.60; N, 9.77.

4.1.24. 2,4,10,10-Tetramethyl-6,8-bis-(4-phenyl)-1-oxa-4,6,8-triazaspiro[4,5]decane-7,9-dione (17c). Compound **17c** consists of two diastereomers. They are (2*R*,5*R*)/(2*S*,5*S*)-2,4,10,10-tetramethyl-6,8-(4-nitrophenyl)-1-oxa-3,6,8-triazospiro[4,5]decane-7,9-dione (**17c**).

Mp 129–133 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.45–7.14 (m, 10H), 4.11(m, 1H), 3.02 (m, 1H), 2.76 (s, 3H), 2.58 (m, 1H), 1.69 (s, 3H), 1.33 (s, 3H), 0.46 (d, J=6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 176.3, 154.1, 137.2, 133.8, 132.5, 132.2, 129.9, 129.7, 129.5, 129.1, 108.1, 76.1, 60.7, 49.1, 34.5, 26.0, 19.7, 18.5. Anal. Calcd for $C_{22}H_{25}O_3N_3$: C, 69.67; H, 6.59; N, 11.08. Found: C, 69.53; H, 6.77; N, 11.21.

4.1.25. (2*S*,5*R*)/(2*R*,5*S*)-2,4,10,10-Tetramethyl-6,8-(4-nitrophenyl)-1-oxa-3,6,8-triazospiro[4,5]decane-7,9-dione (17c). Mp 129–133 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.45–7.14 (m, 10H), 3.30 (m, 1H), 3.02 (m, 2H), 2.76 (s, 3H), 2.70 (m, 1H), 1.69 (s, 3H), 1.33 (s, 3H), 1.12 (d, J=6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 176.3, 154.2, 139.3,

133.8, 132.8, 132.5, 130.3, 129.7, 129.7, 129.1, 108.1, 73.4, 60.5, 48.6, 34.6, 26.2, 22.0, 19.7.

4.1.26. 2,4,10,10-Tetramethyl-6,8-bis-(4-*p*-tolyl)-1-oxa-4,6,8-triazaspiro[4,5]decane-7,9-dione (17d). Compound **17d** consists of two diastereoisomers. They are (2*R*,5*R*)/(2*S*,5*S*)-2,4,10,10-tetramethyl-6,8-(4-*p*-tolyl)-1-oxa-3,6,8-triazospiro[4,5]decane-7,9-dione (**17d**).

Mp 171–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26–7.02 (m, 8H), 4.11 (m, 1H), 3.00 (m, 1H), 2.74 (s, 3H), 2.59 (m, 1H), 2.35 (s, 6H), 1.66 (s, 3H), 1.32 (s, 3H), 0.46 (d, J= 6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 174.7, 152.7, 137.8, 135.2, 132.0, 130.4, 129.5, 129.1, 128.8, 128.0, 106.4, 74.6, 59.3, 47.6, 33.2, 24.6, 21.1, 18.4, 17.1.

4.1.27. (2*S*,5*R*)/(2*R*,5*S*)-2,4,10,10-Tetramethyl-6,8-(4-nitrophenyl)-1-oxa-3,6,8-triazospiro[4,5]decane-7,9-dione (17d). Mp 171–173 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26-7.02 (m, 8H), 3.35 (m, 1H), 3.02 (m, 2H), 2.73 (s, 3H), 2.69 (m, 1H), 2.35 (s, 6H), 1.66 (s, 3H), 1.31 (s, 3H), 1.11 (d, J=6.2 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 174.7, 152.7, 137.4, 136.0, 133.2, 130.4, 129.5, 129.1, 128.8, 128.0, 106.4, 71.8, 59.1, 47.1, 33.1, 24.7, 21.1, 18.3. Anal. Calcd for $C_{24}H_{29}O_3N_3$: C, 70.77; H, 7.12; N, 10.32. Found: C, 70.65; H, 7.31; N, 10.14.

4.1.28. 3,3,4,10,10-Pentamethyl-6,8-bis-(4-nitrophenyl)-1-oxa-4,6,8-triaza-spiro[4,5]decane-7,9-dione (17e). Mp 195–197 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35–8.31 (m, aromatic H, 8H), 3.61 (d, J=8.0 Hz, 1H), 2.85 (d, J= 8.0 Hz, 1H), 2.64 (s, 3H), 1.74 (s, 3H), 1.37 (s, 3H), 1.11 (s, 3H), 0.76 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 174.0, 151.5, 147.8, 147.3, 143.8, 133.7, 132.6, 132.0, 129.7, 123.9, 109.0, 78.1, 59.6, 48.7, 26.4, 25.8, 24.6, 19.0, 14.7. IR (KBr): 2979, 1725, 1675, 1615, 1603, 1530, 1502, 1397, 1335, 1274, 1123, 1023, 833 and 744 cm^{-1}.

4.1.29. 2,4,10,10-Tetramethyl-6,8-bis-(4-nitrophenyl)-1-oxa-4,6,8-triaza-spiro[4,5]decane-7,9-dione (17f). Compound **17f** consists of two diastereomers. They are (2*R*,5*R*)/(2*S*,5*S*)-2,4,10,10-(-tetramethyl-6,8-(4-nitrophenyl)-1-oxa-3,6,8-triazospiro[4,5]decane-7,9-dione (**17f**).

Mp 193–195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–8.31 (m, 8H), 4.17–4.20 (m, 1H), 3.10 (m, 1H), 2.79 (s, 3H), 2.78 (m, 1H), 1.72 (s, 3H), 1.37 (s, 3H), 0.57 (d, J=6.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 174.0, 151.3, 147.1, 144.4, 141.1, 132.4, 131.1, 129.8, 124.3, 123.8, 106.9, 76.8, 59.3, 48.0, 33.4, 24.6, 18.4, 17.5. IR (KBr): 2985, 1735, 1681, 1614, 1530, 1502, 1402, 1335, 1319, 1274, 1190, 1118, 1040, 845, 800, 733 cm^{-1}.

4.1.30. (2*S*,5*R*)/(2*R*,5*S*)-2,4,10,10-Tetramethyl-6,8-(4-nitrophenyl)-1-oxa-3,6,8-triazospiro[4,5]decane-7,9-dione (17f). Mp 193–195 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34–8.31 (m, 8H), 3.39 (m, 1H), 3.09 (m, 2H), 2.78 (s, 3H), 3.00 (m, 1H), 1.72 (s, 3H), 1.35 (s, 3H), 1.16 (d, J= 6.7 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 177.1, 151.6, 147.5, 147.1, 143.5, 133.5, 132.2, 132.0, 129.7, 123.9, 107.1, 75.3, 58.8, 47.7, 33.4, 24.8, 20.2, 18.3. IR (KBr): 2984, 1735, 1679, 1507, 1391, 1327, 1185, 1034, 828, 723, 521 cm^{-1}.

4.1.31. 5,5,11-Trimethyl-1,3-diphenyl-7-oxa-1,3,11-triazaspiro[5,5]undecane-2,4-dione (18a). Mp 138–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43–7.14 (m, 10H), 3.53 (m, 1H), 3.03 (m, 2H), 2.88 (m, 2H), 2.70 (s, 3H), 1.72 (m, 1H), 1.63 (s, 3H), 1.39 (s, 3H), 1.28 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 175.4, 152.5, 138.3, 135.9, 131.3, 128.8, 128.5, 128.3, 128.0, 127.8, 100.4, 61.7, 49.9, 47.5, 37.8, 24.8, 22.9, 20.6, 18.0 cm^{-1}. Anal. Calcd for $C_{22}H_{25}O_3N_3$: C, 69.67; H, 6.59; N, 11.08. Found: C, 69.59; H, 6.77; N, 10.92.

4.1.32. 5,5,11-Trimethyl-1,3-di-*p*-tolyl-7-oxa-1,3,11-triazaspiro[5,5]undecane-2,4-dione (18b). Mp 155–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30–7.01 (m, 8H), 3.53 (m, 1H), 3.00 (m, 2H), 2.87 (m, 2H), 2.67 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 1.71 (m, 1H), 1.60 (s,3H), 1.37 (s, 3H), 1.29 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 175.0, 152.3, 137.3, 137.1, 135.1, 132.7, 130.5, 129.0, 128.7, 127.4, 99.7, 61.3, 49.3, 47.1, 37.4, 24.4, 22.5, 20.6, 17.6. IR (KBr): 2971, 1725, 1688, 1521, 1419, 1326, 1186, 1056, 814, 749, 526 cm^{-1}. Anal. Calcd for $C_{24}H_{29}O_3N_3$: C, 70.77; H, 7.12; N, 10.32. Found: C, 70.54; H, 7.31; N, 10.18.

4.1.33. 1,3,5-Triphenyl-[1,3,5]triazinane-2,4,6-trione (30a). Mp 269–270 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51–7.24 (aromatic H). ^{13}C NMR ($CDCl_3$): δ 148.6, 133.9, 129.3, 129.2, 128.4. MS (CI): Calcd for $C_{21}H_{15}O_3N_3$: 357.4 (M). Found: 358.4 (M+1). IR (KBr): 1717, 1596, 1503, 1429, 1224, 964, 760, 713, 593 cm^{-1}.

4.1.34. 1,3,5-Tri-*p*-tolyl-[1,3,5]triazinane-2,4,6-trione (30b). Mp 281–282 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.26 (aromatic H, 12H), 2.38 (s, 9H). ^{13}C NMR ($CDCl_3$): δ 148.8, 139.2, 131.0, 129.9, 128.0, 21.2. IR (KBr): 1719, 1409, 964, 813, 756, 544 cm^{-1}. Anal. Calcd for $C_{24}H_{21}O_3N_3$: C, 72.19; H, 5.26; N, 10.53. Found: C, 72.26; H, 5.34; N, 10.33.

4.1.35. 1,3,5-Tris-(4-nitrophenyl)-[1,3,5]triazinane-2,4,6-trione (30c). Mp 286 °C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.43–7.76 (aromatic H). ^{13}C NMR ($CDCl_3$): δ 149.2, 148.9, 140.9, 131.3, 125.2. IR (KBr): 2929, 1720, 1525, 1430, 1352, 817, 767 cm^{-1}.

Acknowledgements

Partial support of this work by the National Science Foundation, Grant No. EPS 012618 and by Mississippi State University is acknowledged.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2006.02.011. Crystallographic data (excluding structure factors) for the structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 285465–285468 (**5b**, **6**, **17e**, **30c**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or deposit@ccdc.cam.ac.uk].

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