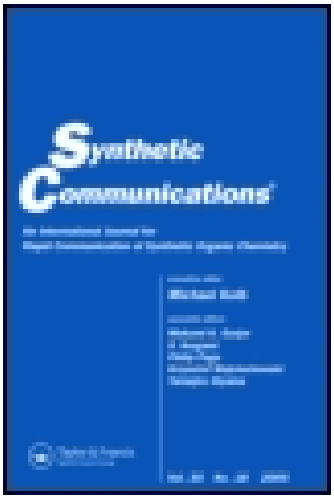


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Efficient and Practical Route to α-Aminocarbonylketene and α-Cyanoketene Dithioacetals

Yanbing Yin [a b], Qian Zhang [a], Qun Liu [a], Yu Liu [a] & Shaoguang Sun [a]
[a] Department of Chemistry, Northeast Normal University, Changchun, China
[b] Department of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar, China
Published online: 10 Mar 2007.

To cite this article: Yanbing Yin, Qian Zhang, Qun Liu, Yu Liu & Shaoguang Sun (2007) Efficient and Practical Route to α-Aminocarbonylketene and α-Cyanoketene Dithioacetals, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 37:5, 703-711, DOI: 10.1080/00397910601131379

To link to this article: http://dx.doi.org/10.1080/00397910601131379

Synthetic Communications®, 37: 703–711, 2007

ISSN 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910601131379

Efficient and Practical Route to α-Aminocarbonylketene and α-Cyanoketene Dithioacetals

Yanbing Yin
Department of Chemistry, Northeast Normal University, Changchun, China and Department of Chemistry and Chemical Engineering, Qiqihar University, Qiqihar, China

Qian Zhang, Qun Liu, Yu Liu, and Shaoguang Sun
Department of Chemistry, Northeast Normal University, Changchun, China

Abstract: An efficient and practical route to α-aminocarbonylketene dithioacetals **5** and α-cyanoketene dithioacetals 6 was developed. With readily available α-acetyl-α-aminocarbonyl ketene dithioacetals **4** as the starting materials, α-aminocarbonylketene dithioacetals **5** were prepared in high yield via base-catalyzed (sodium hydroxide) deacetylation. In the presence of $POCl_3$ and with DMF as the solvent, α-cyanoketene dithioacetals **6** were obtained via dehydration of **5** in excellent yield.

Keywords: α-acetyl-α-aminocarbonyl ketene dithioacetals, α-aminocarbonylketene, α-cyanoketene dithioacetals, deacetylation, dehydration, dithioacetals

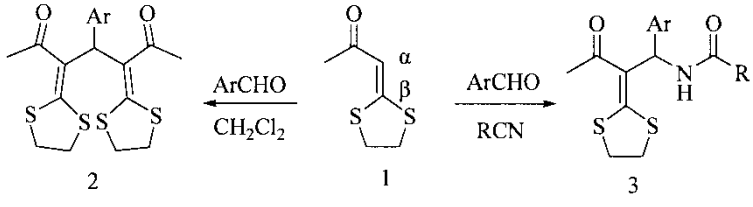
Over the past decades, the utility of α-functionalized ketene dithioacetals as versatile intermediates in organic synthesis has been recognized.[1–3] As part of our studies in this field,[4] recently we became interested in

Received June 20, 2006
Address correspondence to Qian Zhang, Department of Chemistry, Northeast Normal University, Changchun 130024, China. E-mail: zhangq651@nenu.du.cn or Qun Liu, liuqun@nenu.edu.cn

the C-C bond-forming reactions of the polarized ketene dithioacetals toward carbon nucleophiles at their α-position and the reactions of α-acetylketene dithioacetal **1** with reactive arylaldehydes[5a] or **1** with reactive arylaldehydes[5a] or with respective arylaldehydes nitriles[5b] to give the double Morita–Baylis–Hilman type adducts **2** and aza-Mortia–Baylis–Hillman type adducts **3** (Scheme 1), respectively, were reported. In continuing the research, the ketene dithioacetals with different electron-withdrawing groups (EWG) on the α-position were examined for their efficiency in the C-C bond-forming reactions. Thus, the α-cyanoketene dithioacetals with the structure of **6** (Scheme 2) was chosen, because unsaturated nitriles can be expected to show interesting properties in organic synthesis.[6]

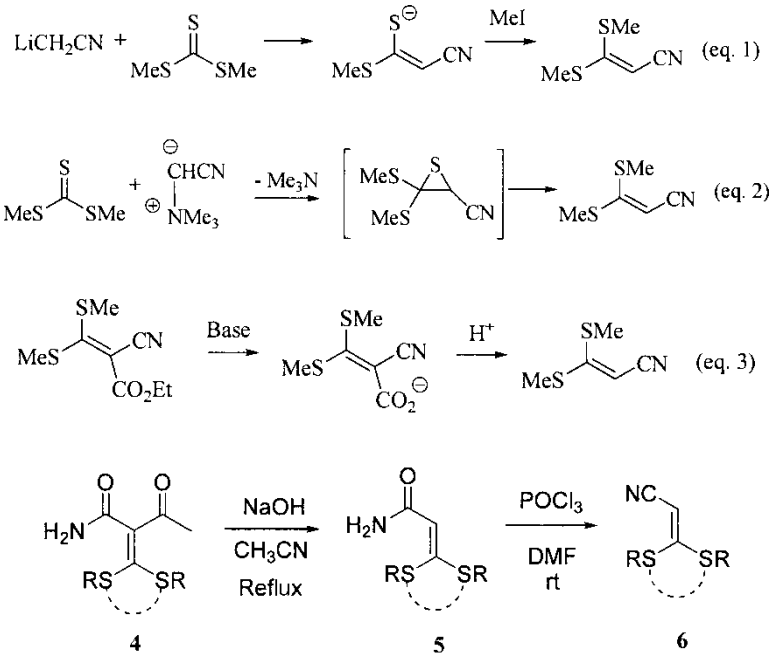
To our knowledge, there are few reports about the synthesis of α-cyanoketene dithioacetals with the structure of **6** (Scheme 2). Among these reported, the reactions of the condensation on the lithium salt of acetonitrile with dimethyl trithiocarbonate followed by alkylation [Eq. (1)][7a] and the reaction of the cyanotrimethylammonium ylid with dialkyl trithiocarbonate [Eq. (2)][7b] were involved. Intrinsic drawbacks, however, such as the low[7a] or unsatisfactory yield (50–58%),[7b] moisture-sensitive reaction conditions, and the use of a separate step for dialkyl trithiocarbonate[7a,7b] or cyanotrimethylammonium methylid[7b] preparation severely limit their application. On the other hand, although the route via the saponification of 3,3-bis(alkylthio)-2-ethoxycarbonylacrylonitrile and subsequent decarboxylation [Eq. (3)] is simple, it suffers from the unspecified product yields.[7c] According to our previous works,[8] the commercially available double-activated ketene dithioacetals (with two EWG at the α-position) were selected as the substrates. The substrates α-acetyl-α-aminocarbonyl ketene dithioacetals **4a**–**4e** were prepared in 78–85% yields according to the literature method.[9] Thus, starting from α-acetyl-α-aminocarbonyl ketene dithioacetals **4** (Scheme 2), a series of α-aminocarbonylketene dithioacetals **5** and α-cyanoketene dithioacetals **6** were synthesized, respectively, in high to excellent yields under mild reaction conditions. The results are described in this communication.

In the beginning of this study, the saponification of 3,3-bis(methylthio)-2-methoxycarbonylacrylonitrile and subsequent decarboxylation method[7c] was reexamined. The results showed that this method did afford the desired product, α-cyanoketene dimethylthioacetal **6a**, but in an unspecified yield



2 1 3

Scheme 1.



Scheme 2. Synthesis of α-aminocarbonyl **5** and α-cyanoketene dithioacetals **6**.

(in the range of 20–50%) because both cyano and methoxycarbonyl groups are sensitive under basic conditions. In fact, amide functionality is more stable than methoxycarbonyl, acetyl, or cyano group to bases and can undergo dehydration to the cyano group by a dehydration reagent. The deacetylation and dehydration sequence was then designed with the easily available α-acetyl-α-aminocarbonyl ketene dithioacetals **4** as the substrates. As a probe experiment, the deacetylation reaction of 2-(bis(methylthio)methylene)-3-oxobutanamide, substrate **4a**, was investigated at first. The reaction completed after the mixture of a **4a** (410 mg, 2.0 mmol) and NaOH (160 mg, 4.0 mmol) in acentonitrile (10 mL) was heated at reflux temperature for 30 min (monitored by thin-layer chromatography, TLC), and then the reaction mixture was poured into cold water (10 mL) and stirred for another 30 min. Pure 3,3-bis(methylthio)acrylamide, product **5a**, was obtained as a light yellow solid in 80% yield simply by filtration. Under identical conditions as those described previously α-aminocarbonylketene dithioacetals **5b**–**5e** were obtained in high yields (Table 1).

With the easily available α-aminocarbonyl ketene dithioacetals at hand, our attention was then turned to their dehydration reaction to prepare the corresponding α-cyanoketene dithioacetals **6**, and $POCl_3$ was adopted as the dehydration reagent.[10] As a result, the dehydration reaction occurred very fast. For example, to the solution of α-aminocarbonyl ketene dithioacetal **5a** (326 mg,

Table 1. Prepared α-aminocarbonylketene dithioacetals **5** and α-cyanoketene dithioacetals **6**

Product **5, 6**	R	Yield (%) **5**	Yield (%) **6**
a	CH_3	80	95
b	CH_3CH_2	78	92
c	$(CH_2)_2$	88	95
d	$(CH_2)_3$	85	93
e	$C_6H_5CH_2$	78	90

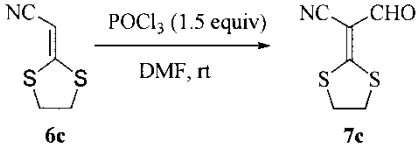
2.0 mmol) in 10 mL of DMF, $POCl_3$ (0.26 mL, 2.4 mmol) was added dropwise within 5 min under stirring at room temperature, and the reaction mixture was stirred for another 5 min at room temperature to completion (monitored by TLC). Then the reaction mixture was poured into cold water (10 mL) and stirred for 10 min. Pure 3,3-bis(methylthio)acrylonitrile, product **6a**, was obtained as a white crystal in 95% yield simply by filtration. Under identical conditions as those described previously, α-cyanoketene dithioacetals **6c**–**6e** were obtained in nearly quantitative yield (Table 1). Compound **6b**, a liquid product, was obtained by extracting the reaction mixture with dichloromethane (10 mL × 2), washing with water, drying over anhydrous magnesium sulfate, and then evaporating the solution (Table 1).

In our experiments, we found that when 1.5 equiv. $POCl_3$ to **6c** was added, a product, 2-(1,3-dithiolan-2-ylidene)-3-oxopropanenitrile **7c**, was obtained in 95% yield. A similar result was also reported by Anabha and coworkers.[11]

In conclusion, we have demonstrated a facile method for the preparation of α-aminocarbonyl and α-cyanoketene dithioacetals. Some advantages, such as the readily available substrates and reagents, mild reaction conditions, and high yields, make this method attractive. The potential synthetic applications of α-cyanoketene dithioacetals are being explored (Scheme 3).

EXPERIMENTAL

All reagents were commercial and were used without further purification. The α-acetyl-α-aminocarbonyl ketene dithioacetals **4a**–**4e** were prepared via a



6c **7c**

Scheme 3. Synhesis of 2-(1,3-dithiolan-2-ylidene)-3-oxopropanenitrille.

known procedure.[9] Anhydrous $MgSO_4$ was used as drying agent. Melting points are uncorrected. The ^1H NMR and ^{13}C spectra were determined on a Varian Unity spectrometer (500 MHz) in $CDCl_3$ with TMS as internal standard. IR (KBr) spectra were measured using a Magna-IR 560 spectrometer. Mass spectra were recorded on Agilient 1100 LCMsD spectrometer. Elemental analyses were obtained on a PE-2400 analyser.

General Procedure

General Procedure for **5**

The corresponding compound **4** (20 mmol) was added to a solution of sodium hydroxide (40 mmol) in acetonitrile (100 mL). The mixture was refluxed for 30 min (monitored by TLC), and then the reaction mixture was poured into cold water (100 mL) and stirred for another 30 min. Pure α-aminocarbonylketene dithioacetals **5** was obtained as a solid simply by filtration.

Data

5a. Yield 80%; light yellow solid; mp 128–130°C; ^1H NMR (500 MHz, $CDCl_3$) δ: 2.38 (s, 3H, SCH_3), 2.47 (s, 3H, SCH_3), 5.61 (s, 1H, C═CH), 5.78 (broad, 2H, NH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 14.82, 16.03, 109.19, 154.69, 165.74; IR (KBr, cm^{-1}): 3347, 2997, 2881, 1643, 1523, 1383, 1264; MS (EI) m/z 164 $[(M+1)]^+$; anal. calcd. for $C_5H_9NOS_2$: C, 36.78; H, 5.56; N, 8.58. Found: C, 36.86; H, 5.68; N, 8.42.

5b. Yield 78%; pale brown solid; mp 100–102°C; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.31–1.35 (m, 6H, CH_3), 2.86 (q, 2H, $J = 7.5$ Hz, SCH_2), 3.01 (q, 2H, $J = 7.5$ Hz, SCH_2), 5.52 (broad, 1H, NH), 5.86 (s, 1H, C═CH), 6.54 (broad, 1H, NH); ^{13}C NMR (125 MHz, $CDC1_3$) δ: 13.14, 14.92, 28.14, 28.28, 116.65, 150.89, 166.69; IR (KBr, cm^{-1}): 3389, 3186, 2928, 1636, 1539, 1380, 1274; MS (EI) m/z 192 $[(M+1)]^+$; anal. calcd. for $C_7H_{13}NOS_2$: C, 43.95; H, 6.85; N, 7.32. Found: C, 44.08; H, 6.77; N, 7.25.

5c. Yield 88%; pale brown solid; mp 162–164°C; ^1H NMR (500 MHz, $CDC1_3$) δ: 3.34 (t, 2H, $J = 6.0$ Hz, SCH_2), 3.42 (t, 2H, $J = 6.0$ Hz, SCH_2), 5.22 (broad, 2H, NH_2), 6.08 (s, 1H, C═CH); ^{13}C NMR (125 MHz, $CDC1_3$) δ: 35.74, 38.92, 104.78, 161.73, 167.28; IR (KBr, cm^{-1}): 3391, 3168, 1638, 1553, 1386, 1266; MS (EI) m/z 162 $[(M+1)]^+$; anal. calcd. for $C_5H_7NOS_2$: C, 37.24; H, 4.38; N, 8.69. Found: C, 37.15; H, 4.49; N, 8.58.

5d. Yield 85%; pale brown solid; mp 154–156°C; ^1H NMR (500 MHz, $CDCl_3$) δ: 2.18–2.21 (m, 2H, CH_2), 2.95–2.99 (m, 4H, SCH_2), 5.38

(broad, 2H, NH_2), 6.11 (s, 1H, C═CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 23.82, 28.14, 28.77, 114.80, 156.68, 166.85; IR (KBr, cm^{-1}): 3395, 3208, 1652, 1540, 1381, 1271; MS (EI) m/z 176 $[(M+l)]^+$; anal. calcd. for $C_6H_9NOS_2$: C, 41.12; H, 5.18; N, 7.99. Found: C, 41.26; H, 5.30; N, 7.91.

5e. Yield 78%; brown solid; mp 138–140°C; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.05 (s, 2H, CH_2), 4.17 (s, 2H, CH_2), 5.25 (broad, 1H, NH), 5.94 (s, 1H, C═CH), 6.07 (broad, 1H, NH), 7.25–7.37 (m, 10 H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 38.77, 39.09, 119.34, 127.92, 128.08, 128.97, 129.08, 129.25, 129.27, 135.12, 136.72, 149.08, 166.29; IR (KBr, cm^{-1}): 3481, 3150, 1650, 1518, 1375, 1274, 1069; MS (EI) m/z 316 $[(M+l)]^+$; anal. calcd. for $C_{17}H_{17}NOS_2$: C, 64.73; H, 5.43; N, 4.44. Found: C, 64.84; H, 5.51; N, 4.36.

General Procedure for **6**

To the solution of α-aminocarbonyl ketene dithioacetal **5a** (20 mmol) in 50 mL of DMF, $POCl_3$ (24 mmol) was added dropwise within 5 min under stirring at room temperature, and the reaction mixture was stirred for another 5 min at room temperature (monitored by TLC). Then the reaction mixture was poured into cold water (50 mL) and stirred for 10 min. Pure α-cyanoketene dithioacetals **6** (except **6b**) were obtained as white crystals simply by filtration. Compound **6b**, a liquid product, was obtained by extracting the reaction mixture with dichloromethane (25 mL × 2), washing with water, drying over anhydrous magnesium sulfate, and evaporating the solution.

Data

6a. Yield 95%; white crystal; mp 30–32°C; ^1H NMR (500 MHz, $CDC1_3$) δ: 2.41 (s, 3H, SCH_3), 2.56 (s, 3H, SCH_3), 5.02 (s, 1H, C═CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 15.34, 15.97, 86.32, 115.34, 163.43; IR (KBr, cm^{-1}): 3083, 2991, 2197, 1510, 1419, 1271, 1051, 918; MS (EI) m/z 146 $[(M+l)]^+$; anal. calcd. for $C_5H_7NS_2$: C, 41.35; H, 4.86; N, 9.64. Found: C, 41.48; H, 4.75; N, 9.57.

6b. Yield 92%; pale yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ: 1.31–1.34 (m, 6H, CH_3), 2.87 (q, 2H, $J = 7.5$ Hz, SCH_2), 3.04 (q, 2H, $J = 7.5$ Hz, SCH_2), 5.18 (s, 1H, C═CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 13.12, 14.96, 28.41, 28.45, 90.74, 116.69, 162.22; IR (KBr, cm^{-1}): 2973, 2930, 2204, 1522, 1450, 1377, 1262, 1056, 920; MS (EI) m/z 174 $[(M+1)]^+$; anal. calcd. for $C_7H_{11}NS_2$: C, 48.51; H, 6.40; N, 8.08. Found: C, 48.63; H, 6.52; N, 8.13.

6c. Yield 92%; white crystal; mp 54–56°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.55–3.59 (m, 4H, SCH_2), 5.30 (s, 1H, C═CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 38.31, 38.50, 80.28, 116.60, 167.38; IR (KBr, cm^{-1}): 2195, 1533, 1421, 1280, 922; MS (EI) m/z 144 $[(M+1)]^+$; anal. calcd. for $C_5H_5NS_2$: C, 41.93; H, 3.52; N, 9.78. Found: C, 42.02; H, 3.64; N, 9.85.

6d. Yield 93%; white crystal; mp 60–62°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.17–2.24 (m, 2H, CH_2), 2.97–3.06 (m, 4H, SCH_2), 5.36 (s, 1H, C═CH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 22.84, 28.77, 28.87, 90.19, 116.43, 164.16; IR (KBr, cm^{-1}): 2924, 2200, 1525, 1420, 1302, 912; MS (EI) m/z 158 $[(M+1)]^+$; anal. calcd. for $C_6H_7NS_2$: C, 45.83; H, 4.49; N, 8.91. Found: C, 45.91; H, 4.56; N, 8.85.

6e. Yield 90%; white crystal; mp 76–78°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 4.03 (s, 2H, CH_2), 4.25 (s, 2H, CH_2), 5.25 (s, 1H, C = CH) 7.27–7.37 (m, 10H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 38.92, 39.31, 93.95, 116.31, 128.06, 128.35, 128.93, 129.02, 129.24, 129.37, 134.32, 135.84, 160.85; IR (KBr, cm^{-1}): 2199, 1645, 1538, 1501, 1454, 1236, 1070; MS (EI) m/z 298 $[(M+1)]^+$; anal. calcd. for $C_{17}H_{15}NS_2$: C, 68.65; H, 5.08; N, 4.71. Found: C, 68.78; H, 5.19; N, 4.68.

General Procedure for **7c**

To the solution of 2-(1,3-dithiolan-2-ylidene)acetonitrile **6c** (4 mmol) in 5 mL of DMF, $POCl_3$ (6 mmol) was added dropwise under stirring at 0°C, and the reaction mixture was stirred for 24 h at room temperature (monitored by TLC). Then the reaction mixture was poured into a cold sat. K_2CO_3 solution (60 mL). The pure product 2-(1,3-dithiolan-2-ylidene)-3-oxopropanenitrile **7c** was obtained as a white solid simply by filtration.

Data

7c. Yield 95%; white solid; mp 116–118°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.57–3.69 (m, 4H, SCH_2), 9.46 (s, 1H, CHO); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 35.54, 39.46, 96.86, 116.00, 180.73, 180.60; IR (KBr, cm^{-1}C): 2197, 1652, 1425, 1210, 1015; MS (EI) m/z 172 $[(M+1)]^+$; anal. calcd. for $C_6H_5NOS_2$: C, 42.08; H, 2.94; N, 8.18. Found: C, 42.25; H, 3.08; N, 8.11.

ACKNOWLEDGMENTS

Financial support of this by the National Natural Science Foundation of China (NNSFC) (20272008) and the Key Grant Project of Chinese Ministry of Education (10412) are greatly acknowledged.

REFERENCES

1. For review; on the synthesis and application of α-oxo ketene dithioacetals, see (a) Dieter, R. K. α-Oxo ketene dithioacetals and related compounds: Versatile three-carbon synthons. *Tetrahedron* **1986**, *42*, 3029–3096; (b) Tominga, Y. Synthesis of heterocyclic compounds using carbon disulfide and their products. *J. Heterocycl. Chem.* **1989**, *26*, 1167–1204; (c) Junjappa, H.; Ila, H.; Asokan, C. V. α-Oxoketene-S,S-, N,S- and N,N-acetals: intermediates in organic synthesis Tetrahedron **1990**, *46*, 5423–5506; (d) Kolb, M. Ketene dithioacetals in organic synthesis: Recent developments. *Synthesis* **1990**, *3*, 171–190; (e) Junjappa, H.; Ila, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *35*, 95–96; (f) Junjappa, H.; Ila, H.; Mohanta, P. K. In *Progress in Heterocyclic Chemistry*; Gribble, G. H., Gilchrist, L. T., Eds.; Pergamon Press: Oxford, 2001, 13, Chapter 1, pp. 1–24.
2. Selected examples of phosphonoketen dithioacetals (a) Kouno, R.; Okauchi, T.; Nakamura, M.; Ichikawa, J.; Minami, T. Synthesis and synthetic utilization of α-functionalized vinylphosphonates bearing β-oxy or β-thio substituents. *J. Org. Chem.* **1998**, *63*, 6239–6246: (b) Minami, T.; Okauchi, T.; Matsuki, H.; Nakamura, M.; Ichikawa, J.; Ishida, M. Synthesis and synthetic application of phosphonoketene dithioacetals: New synthesis of dithioallenes and (α-dithiocarboxyvinyl)phosphonates. *J. Org. Chem.* **1996**, *61*, 8132–8140.
3. Selected examples of fluorinated ketene dithioacetals (a) Brulé, C.; Bouillon, J.- P.; Nicolaï, E.; Portella, C. Fluorinated ketene dithioacetals, part 10: Synthesis of new perfluorinated (2*H*)-pyridazin-3-ones and 3-(alkyl- or arylamino) substituted pyridazines. *Synthesis* **2003**, *3*, 436–442; (b) Timoshenko, V. M.; Bouillon, J.- P.; Shermolovich, Y. G.; Portella, C. Flourinated ketene dithioacetals, part IX: Synthesis and some chemical properties of new fluorinated 3*H*-1,2-dithiole-3-thiones. *Tetrahedron Lett.* **2002**, *43*, 5809–5812; (c) Pfund, E.; Masson, S.; Vazeux, M.; Lequeux, T. Syntheses of α-fluoro-α,β-unsaturated thioamides and thiazolines from a fluorophosphonodithioacetate. *J. Org. Chem.* **2004**, *69*, 4670–4676.
4. (a) Liu, Q.; Che, G.; Yu, H.; Liu, Y.; Zhang, J.; Zhang, Q.; Dong, D. The first non-thiolic, odorless 1,3-propanedithiol equivalent and its application in thioacetalization. *J. Org. Chem.* **2003**, *68*, 9148–9150; (b) Yu, H.; Liu, Q.; Yin, Y.; Fang, Q.; Zhang, J.; Dong, D. α,α-Diacetyl cyclic ketene dithioacetals: Odorless and efficient dithiol equivalents in thioacetalization reaction. *Synlett* **2004**, *6*, 999–1002; (c) Dong, D.; Bi, X.; Liu, Q.; Cong, F. [5C + 1 N] Annulation: A novel synthetic strategy for functionalized 2,3-dithydro-4-pyridones. *Chem. Commun.* **2005**, *28*, 3580–3582; (d) Bi, X.; Dong, D.; Liu, Q.; Pan, W.; Zhao, L.; Li, B. [5 + 1] Annulation: A synthetic strategy for highly substituted phenols and cyclohexenones. *J. Am. Chem. Soc* **2005**, *127*, 4578–4579; (e) Wang, M.; Ai, L.; Zhang, J.; Liu, Q.; Gao, L. Synthesis of 2-benzylthio-5-phenyl-3,4-disubstituted thiophenes by intramolecular condensation of α-oxo ketene dibenzyl-thioacetals. *Chin. J. Chem.* **2002**, *20*, 1591–1597; (f) Zhang, S.; Liu, Q.; Chen, Y. Studies on the one-pot reaction of active methylene compounds with 2-bromoethanol—Preparation of α-oxoketene cyclic O,S-ethylene acetals. *Ind. J. Chem.* **2000**, *39B*, 147–150.
5. (a) Yin, Y.; Wang, M.; Liu, Q.; Hu, J.; Sun, S.; Kang, J. A C-C bond formation reaction at the α-carbon atom of α-oxo ketene dithioacetals via the Baylis–Hillman type reaction. *Tetrahedron Lett.* **2005**, *46*, 4399–4402; (b) Sun, S.; Zhang, Q.; Liu, Q.; Yin, Y.; Li, D.; Dong, D. One-pot synthesis of

aza-Morita–Baylis–Hilman adducts from α-oxo ketene-S,S-acetals arylaldehydes and nitriles. *Tetrahedron Lett.* **2005**, *46*, 6271–6274.

6. Review: Fleming, F. F.; Wang, Q. Unsaturated nitriles: Conjugate additions of carbon nucleophiles to a recalcitrant class of acceptors. *Chem. Rev.* **2003**, *103*, 2305–2077.
7. (a) Hartke, K.; Gunther, O. Thion- und Dithioester, XI: Kondensation von Acetonitril mit Thiocarbonsre-O-estern und Dithiocarbondreestern. *Justus Liebigs Ann. Chem.* **1973**, 1637–1643; (b) Bhattacharjee, S. S.; Ila, H.; Junjappa, H. Cyanotrimethylammonium methylid, formation and reaction with α,β-unsaturated carbonyl compounds: Novel cyclopropanation with an ammonium ylid. *Synthesis* **1982**, *4*, 301–302; (c) Kendall, J. D.; Edwards, H. D. *U.S. Patent* 2,493,071, (1950)*Chem. Abstr.* **1950**, *44*, 7347.
8. (a) Zhang, S.; Liu, Q.; Zhu, Z.; Zhang, C.; Huang, H. Studies on the basic assisted decomposition of α,α-dioxo(ester) ketene dithioacetals. *Chem. J. Chin. Univ.* **1994**, *15*, 1155–1158; (b) Fang, Q.; Liu, Q.; Hu, Y.; Lin, C. A new method for the synthesis of α-aroyl ketene dithioacetals. *Chem. J. Chin. Univ.* **1995**, *16*, 1896–1898.
9. Ouyang, Y.; Dong, D.; Yu, H.; Liang, Y.; Liu, Q. A clean facile and practical synthesis of α-oxoketene S,S-acetals in water. *Adv. Synth. Catal.* **2006**, *348*, 206–210.
10. Zhao, L.; Liang, F.; Bi, X.; Sun, S.; Liu, Q. Efficient synthesis of highly functionalized dihydropyrido[2,3-*d*]pyrmidines by a double annulation strategy from α-alkenoyl-α-carbamoyl ketene-(S,S)-acetals. *J. Org. Chem.* **2006**, *71*, 1094–1098.
11. Anabha, E. R.; Asokan, C. V. A Convenient preparation of 2-aroyl-3,3-bis(alkylsulfanyl)acrylaldehydes and their application in the synthesis of 5-aroyl-2-oxo-1,2-dihydro-2-pyrdinecarbonitriles. *Synthesis* **2006**, *1*, 151–155.