An unprecedented tandem 1,3-dipolar cycloaddition–cheletropic elimination: a facial approach to novel push–pull olefins

Qing Zhu, Mei-Fang Liu, Bo Wang and Ying Cheng*

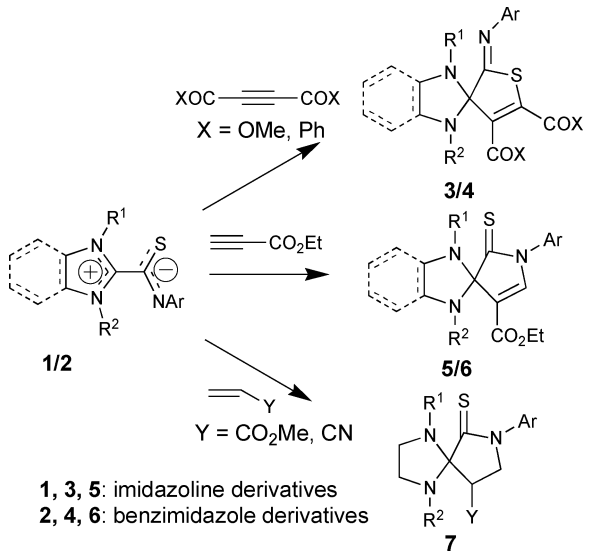
Received 29th January 2007, Accepted 6th March 2007
First published as an Advance Article on the web 20th March 2007
DOI: 10.1039/b701326d

The interaction of 2-(phenylthiocarbamoyl) imidazolium inner salts with dimethyl acetylenedicarboxylate produced dimethyl 2-(imidazolin-2-ylidene)-3-thioxobutanedioates in moderate to good yields. The process involved a tandem reaction comprising a 1,3-dipolar cycloaddition and an unprecedented cheletropic elimination of the phenyl isonitrile from a 2-phenyliminodihydrothiophene moiety. NMR and X-ray diffraction studies confirmed that the 2-(imidazolin-2-ylidene)-3-thioxobutanedioates are novel push–pull olefins and have potential applications in nonlinear optical materials.

Introduction

Modern synthetic design demands high efficiency in terms of minimization of synthetic steps and maximization of complexity of the products. Tandem reactions, which link several transformations together in a single operation, offer a wide range of possibilities for construction of highly complex compounds in one synthetic step. Tandem reactions are thus one of the most valuable strategies in organic synthesis,[1a] and have been widely used in elaboration of multifunctional compounds and natural products.[1b] Pericyclic–pericyclic sequences constitute an important branch of tandem reactions.[1a] For example, tandem cheletropic elimination–Diels–Alder cycloaddition reactions have been successfully applied in the total syntheses of estra-1,3,5(10)-trien-17-one[2] and lycorine,[3] and in assembling other polycyclic molecules.[4] A tandem Diels–Alder–1,3-dipolar reaction has been the key step in the total syntheses of alkaloids vindorosine and minovine.[5] Although numerous tandem reactions have been documented in the literature, few cascade 1,3-dipolar cycloaddition–cheletropic elimination processes have been reported.

Imidazole, imidazoline and benzimidazole carbenes or their dimers were reported to react with isothiocyanates to form 1 + 1 adducts 2-arylthiocarbamoyl imidazolium,[6a] imidazolinium[6b,c] and benzimidazolium inner salts[6d] or the 1 + 2 adducts, dithiohydantoins[6c,7] under different reaction conditions. Recently, we found that the imidazoline and benzimidazole carbene derived 2-arylthiocarbamoyl imidazolinium **1** and benzimidazolium inner salts **2** were unique ambident C^+–C–S^- and C^+–C–N^- 1,3-dipoles.[8] They behaved as C–C–S dipoles undergoing highly efficient and site selective cycloaddition with dimethyl acetylenedicarboxylate (DMAD) or dibenzoylacetylene to furnish spiro[imidazole-2,3′-thiophene] derivatives **3** or **4** in excellent yields. On reacting with ethyl propiolate, methyl acrylate or acrylonitrile, they acted as C–C–N dipoles to give spiro[imidazole-2,3′-pyrrole] derivatives **5**, **6** or **7** in good yields (Scheme 1). In order to study the reactivity and selectivity of various 1,3-dipoles derived from *N*-heterocyclic carbenes, we undertook a study of the interaction of imidazole carbene-derived 2-arylthiocarbamoyl imidazolium inner salts with DMAD. Interestingly, instead of formation of the expected spiro heterocyclic compounds, novel push–pull olefins were obtained in good yields. The formation of the products was the result of an unprecedented tandem 1,3-dipolar cycloaddition–cheletropic elimination reaction.



Scheme 1 Reaction of 2-arylthiocarbamoyl imidazolinium **1** and benzimidazolium inner salts **2** with electron-deficient alkenes and alkynes.

Results and discussion

In this work, imidazole carbenes **9** were generated *in situ* by deprotonation of the corresponding imidazolium **8** salts using sodium hydride at 20–30 °C. All of the *N*,*N*′-dialkylimidazole carbenes reacted with phenyl isothiocyanates to form stable 2-phenylthiocarbamoyl imidazolium inner salts **10** as sole products in good yields (Scheme 2 and Table 1). At ambient temperature, the reaction of dipoles **10** with DMAD in THF proceeded smoothly and rapidly to produce yellow crystalline products, dimethyl 2-(imidazolin-2-ylidene)-3-thioxobutanedioates **11**, in 60–78% (Scheme 3). As indicated in Table 2, the substituents on

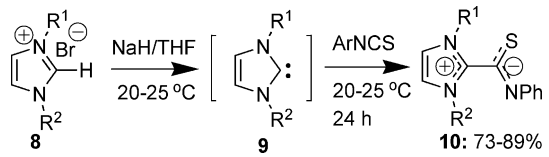
Chemistry Department, Beijing Normal University, Beijing, 100875, China. E-mail: ycheng2@bnu.edu.cn; Fax: +86-10-58802075; Tel: +86-10-58805558

Table 1 Preparation of 2-phenylthiocarbamoyl imidazolium salts **10**

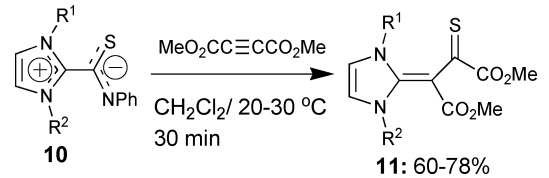
Entry	Starting material **8**: R^1, R^2	Product	Yield (%)
1	**8a**: Et, Et	**10a**	78
2	**8b**: *i*-Pr, *i*-Pr	**10b**	85
3	**8c**: *n*-Bu, *n*-Bu	**10c**	76
4	**8d**: *i*-Pr, *n*-Bu	**10d**	80
5	**8e**: Bn, Bn	**10e**	85
6	**8f**: Et, Bn	**10f**	80
7	**8g**: *i*-Pr, Bn	**10g**	73
8	**8h**: *n*-Bu, Bn	**10h**	89

Table 2 Reaction of 2-phenylthiocarbamoyl imidazolium salts **10** with DMAD

Entry	Starting material **10**: R^1, R^2	Product	Yield (%)
1	**10a**: Et, Et	**11a**	69
2	**10b**: *i*-Pr, *i*-Pr	**11b**	62
3	**10c**: *n*-Bu, *n*-Bu	**11c**	71
4	**10d**: *i*-Pr, *n*-Bu	**11d**	74
5	**10e**: Bn, Bn	**11e**	60
6	**10f**: Et, Bn	**11f**	78
7	**10g**: *i*-Pr, Bn	**11g**	61
8	**10h**: *n*-Bu, Bn	**11h**	73



Scheme 2 Preparation of 2-phenylthiocarbamoyl imidazolium inner salts **10**.



Scheme 3 Reaction of 2-phenylthiocarbamoyl imidazolium inner salts with DMAD.

the dipoles **10** have negligible effect on the outcome of the reaction. The compounds **11** were fully characterized by spectroscopic data and microanalysis, which indicated that they were the 1 + 1 combination of molecules of **10** and DMAD with loss of a PhNC or PhCN moiety. To identify the products beyond doubt, the structure of **11g** was determined unambiguously by single crystal X-ray diffraction analysis (Fig. 1).[9]

Having considered the cycloaddition reaction of 2-arylthiocarbamoyl imidazolinium **1** and benzimidazolium inner salts **2** with DMAD (Scheme 1),[8] the mechanism for the formation of product **11** can be best explained by a tandem 1,3-dipolar cycloaddition–cheletropic elimination reaction. The 2-phenylthiocarbamoyl imidazolium salts **10** acted specifically as C–C–S dipoles toward DMAD to produce cycloaddition intermediates, spiro[imidazole-2,3′-thiophenes] **12**, which underwent cheletropic elimination of phenyl isonitrile from the 2-imino-2,3-dihydrothiophene moiety to afford the products **11** (Scheme 4). In the reaction, the isolation of phenyl isonitrile as a by-product, which

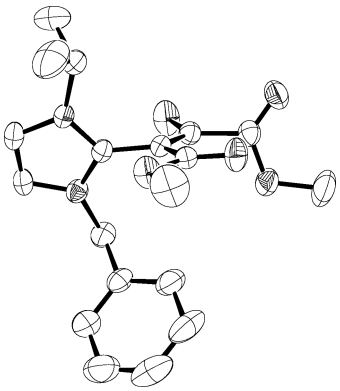
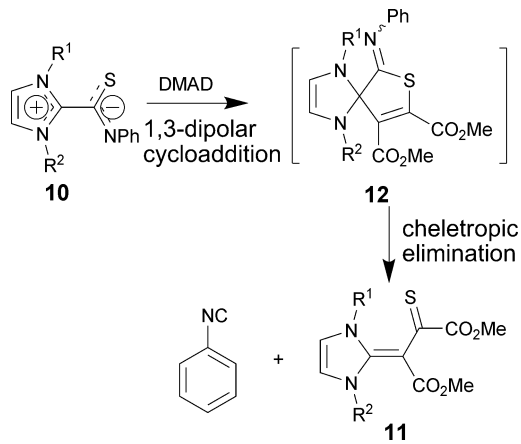


Fig. 1 The ORTEP drawing of single-crystal structure of compound **11g** (50% probability was chosen for the ellipsoids).



Scheme 4

has been identified by comparing the IR spectrum with that of the authentic sample, further supported this mechanism.

To compare the current study with our previous reports,[8] it was found that all the 2-phenylthiocarbamoyl imidazolium **10**, imidazolinium **1** and benzimidazolium inner salts **2** have similar reactivity toward DMAD as all reactions proceeded quickly and efficiently at room temperature. In addition, all reactions have the same site selectivity triggered by the addition of C–C–S dipolar species to DMAD. However, the products derived from 1,3-dipolar cycloaddition of imidazolinium **1**, benzimidazolium **2**, and imidazolium salts **10** with DMAD seem to have quite different stabilities. For example, both spiro products **3** and **4** derived from imidazolinium **1** and benzimidazolium salts **2** are stable compounds, however, the spiro intermediates **12** have never been isolated under the reaction conditions. The reason for the different stabilities is not very clear at this stage. Possibly, the spiro system of **12** has higher ring strains than that of **3** or **4**. The formation of an aromatic imidazoline cation of **11** (see Fig. 2) might be another driving force for the transformation of **12** to **11.**

Cheletropic elimination is an important method for the generation of 1,3-dienes from a five-membered cyclic precursor. The most synthetically useful cheletropic elimination is extrusion of sulfur dioxide from sulfolene dioxides,[2,3,10] although examples of extrusion of nitrogen from diazenes,[11] elimination of carbon monoxide[11b,12] or nitrosobenzene[13] from bridged cyclic compounds are also known. To our knowledge, however, no cheletropic

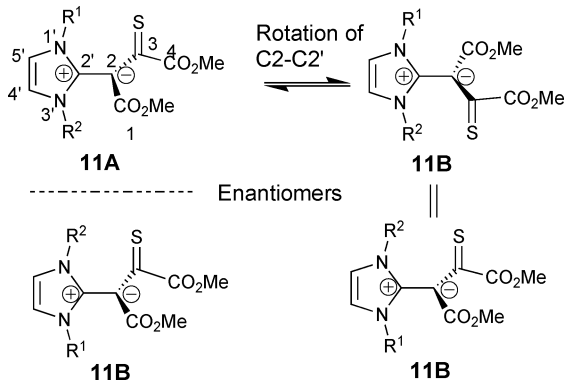


Fig. 2

elimination of an isonitrile from a 2-iminodihydrothiophene derivative has been reported previously.

Push–pull alkenes[14] have attracted much attention for their special molecular structures,[15] physical properties,[16] and potential applications in nonlinear optical materials.[17] Imidazolidinylidene and benzimidazolinylidene substituted ketones, esters and nitriles constituted a small branch of push–pull alkenes.[18] Consideration of the structures, 2-(imidazolin-2-ylidene)-3-thioxobutanedioates **11** can be regarded as a new type of push–pull olefins. Indeed, both ^{13}C NMR spectra and the X-ray diffraction analysis have confirmed the push–pull characteristics of **11**. For example, in the ^{13}C NMR spectra of **11**, C-2 signals of the double bond appeared between 99–100 ppm while C-2′ resonated downfield in the range of 145–147 ppm (The numbering of atoms of **11** is shown in Fig. 2.) The $\Delta\delta$ C=C is about 45–47 ppm. The X-ray diffraction showed that the N1′–C2′ and C2–C3 single bond lengths of **11g** are 1.340 and 1.377 Å, respectively, which were similar to the bond length of C4′–C5′ double bond (1.337 Å). On the contrary, however, the C2–C2′ double bond length is 1.468 Å, being in the range of normal single bond lengths. All of these data indicated the C2–C2′ double bonds of compounds **11** were highly polarized. In the un-symmetrically substituted compounds **11d**, **f**, **g**, **h**, no *Z* and *E* isomers were detected, and no rotational isomerization was observed in their ^{1}H NMR spectra recorded from −70 to 25 °C. This appearance can be explained by the single crystal molecular structure of **11g**, which indicated that the substituents attached respectively to C2 and C2′ are almost in two perpendicular planes (Fig. 1). Therefore, the *Z* and *E* isomers of **11** are conformational isomers (Fig. 2).

Conclusions

In conclusion, we have shown that the reaction of 2-phenylthiocarbamoyl imidazolium inner salts **10** with dimethyl acetylenedicarboxylate proceeded rapidly and efficiently to give dimethyl 2-(imidazolin-2-ylidene)-3-thioxobutanedioates **11** in moderate to good yields. The formation of product **11** can be best explained by a tandem reaction pathway, which comprised a 1,3-dipolar cycloaddition and an unprecedented cheletropic elimination of phenyl isonitrile from a 2-phenyliminodihydrothiophene moiety. The 2-(imidazolin-2-ylidene)-3-thioxobutanedioates are a new type of push–pull olefin, and their push–pull characteristics were proved by both ^{13}C NMR spectroscopy and X-ray diffraction analysis. This work not only enriches the chemistry of cheletropic elimination, but also provides a very simple approach to novel push–pull olefins with potential application as nonlinear optical materials.

Experimental

Melting points are uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded on a Bruker Avance 500 spectrometer. *J* values are reported in Hz. IR spectra were recorded using an AVATAR 360 FT-IR spectrometer. Mass spectra were recorded on a Trace MS (EI) or Surveyor MSQ Plus (ESI) instrument and elemental analyses were performed on a GMBH Vario EL instrument.

1. General procedure for preparation of 2-phenylthiocarbamoyl imidazolium inner salts 10

At ambient temperature, the imidazolium chloride (5 mmol) was mixed with phenyl isothiocyanate (5 mmol) in dry THF (50 cm^3). Under nitrogen atmosphere, NaH (7.5 mmol, 50% in mineral oil) was added in portions to the mixture at 10–15 °C. The resulting mixture was then stirred for 12 h at 10–15 °C. After the reaction, the remaining sodium hydride was quenched by adding water (10 cm^3) dropwise. The solvent was removed and the residue was extracted with dichloromethane (50 × 3 cm^3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated to give 2-thiocarbamoyl imidazolium inner salts **10** as yellow crystals. The products **10** were further purified by recrystallization from dichloromethane and petroleum ether (30–60 °C).

1,3-Diethyl-2-*N*-phenylthiocarbamoyl imidazolium inner salt (10a). 78%, mp 85–86 °C; ν_{max}/cm^{-1} 3131, 1589, 1522 and 1501; δ_H ($CDCl_3$) 7.54 (d, *J* 6.5, 2H, *o*-Ph-H), 7.42 (t, *J* 7.8, 2H, *m*-Ph-H), 7.14 (t, *J* 7.3, 1H, *p*-Ph-H), 7.01 (s, 2H, imidazolinyl-H), 4.38 (q, *J* 7.4, 4H, 2 × N-CH_2CH$_3$), 1.60 (t, *J* 7.4, 6H, 2 × NCH$_2$CH_3); δ_C ($CDCl_3$) 167.3, 149.7, 146.2, 128.6, 124.0, 122.2, 118.2, 43.8, 15.1; EI-MS *m*/*z* 77 (100), 135 (75), 258 (M$^+$, 80), 259 (M + 1, 78%). Anal. Calcd for $C_{14}H_{17}N_3S$: C 64.83, H 6.61, N 16.20; Found: C 65.06, H 6.93, N 15.94%.

1,3-Di(isopropyl)-2-*N*-phenylthiocarbamoyl imidazolium inner salt (10b). 85%, mp 185–186 °C; ν_{max}/cm^{-1} 3159, 3133, 1592, 1521, 1494 and 1480; δ_H (CD_3OD) 7.65 (s, 2H, imidazolinyl-H), 7.37 (t, *J* 8.1, 2H, *m*-Ph-H), 7.25 (d, *J* 7.4, 2H, *o*-Ph-H), 7.11 (t, *J* 7.4, 1H, *p*-Ph-H), 4.97 (m, 2H, 2 × NC*H*(CH$_3$)$_2$), 1.61 (d, *J* 6.7, 12H, 4 × NCH(CH_3)$_2$); δ_C ($CDCl_3$) 167.1, 151.1, 146.0, 128.6, 123.4, 122.1, 115.1, 50.6, 22.7; EI-MS *m*/*z* 134 (100), 287 (M$^+$, 70), 288 (M + 1, 35%). Anal. Calcd for $C_{16}H_{21}N_3S$: C 66.86, H 7.36, N 14.62; Found: C 66.83, H 7.56, N 14.49%.

1,3-Dibutyl-2-*N*-phenylthiocarbamoyl imidazolium inner salt (10c). 76%, mp 115–116 °C; ν_{max}/cm^{-1} 3107, 1593, 1528 and 1497; δ_H ($CDCl_3$) 7.37–7.42 (m, 4H, *o*-Ph-H + *m*-Ph-H), 7.10 (t, *J* 6.9, 1H, *p*-Ph-H), 6.94 (s, 2H, imidazolinyl-H), 4.33 (t, *J* 7.6, 4H, 2 × N-CH_2CH$_2$CH$_2$CH$_3$), 1.95 (quintet, *J* 7.5, 4H, 2 × N-CH$_2$CH_2CH$_2$CH$_3$), 1.45 (sextet, *J* 7.6, 4H, 2 × N-CH$_2$CH$_2$CH_2CH$_3$), 0.98 (t, *J* 7.4, 6H, 2 × N-CH$_2$CH$_2$CH$_2$CH_3); δ_C ($CDCl_3$) 166.6, 151.1, 147.0, 128.6, 123.5, 122.0, 118.4, 48.6, 31.8, 19.8, 13.6; EI-MS *m*/*z* 135 (75), 282 (90), 315 (M$^+$, 100%). Anal. Calcd for $C_{18}H_{25}N_3S$: C 68.53, H 7.99, N 13.32; Found: C 68.34, H 7.95, N 13.04%.

1-Butyl-3-isopropyl-2-*N*-phenylthiocarbamoyl imidazolium inner salt (10d). 80%, mp 144–145 °C; ν_{max}/cm^{-1} 3109, 1593, 1515, 1492 and 1477; δ_H ($CDCl_3$) 7.41 (br s, 4H, *o*-Ph-H + *m*-Ph-H), 7.11 (br s, 1H, *p*-Ph-H), 7.03 (d, *J* 1.2, 1H, imidazolinyl-H), 6.97 (s, 1H, imidazolinyl-H), 5.25 (br, 1H, NC*H*$(CH_3)_2$), 4.30 (t, *J* 7.6, 2H, N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.97 (quintet, *J* 7.7, 2H, N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.59 (d, *J* 6.7, 6H, NCH(C*H*$_3$)$_2$), 1.46 (sextet, *J* 7.6, 2H, N-CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.00 (t, *J* 7.4, 3H, N-CH$_2$CH$_2$CH$_2$C*H*$_3$); δ_C ($CDCl_3$) 166.8, 151.0, 146.7, 128.6, 123.5, 122.1, 118.7, 114.5, 50.8, 48.4, 31.8, 22.8, 19.9, 13.6; EI-MS *m*/*z* 77 (100), 135 (75), 301 (M$^+$, 75), 302 (M + 1, 45%). Anal. Calcd for $C_{17}H_{23}N_3S$: C 67.74, H 7.69, N 13.94; Found: C 67.62, H 7.82, N 13.76%.

1,3-Dibenzyl-2-*N*-phenylthiocarbamoyl imidazolium inner salt (10e). 85%, mp 191–192 °C; ν_{max}/cm^{-1} 3051, 1592, 1535 and 1497; δ_H ($CDCl_3$) 7.51 (d, *J* 5.9, 4H, Ph-H), 7.41–7.45 (m, 10H, Ph-H), 7.11 (t, *J* 7.0, 1H, Ph-H), 6.69 (s, 2H, imidazolinyl-H), 5.52 (s, 4H, 2 × NC*H*$_2$Ph); δ_C ($CDCl_3$) 166.4, 150.6, 147.1, 133.4, 129.30, 129.27, 129.2, 128.7, 123.8, 122.2, 118.4, 52.1; EI-MS *m*/*z* 135 (100), 169 (35), 247 (35), 383 (M$^+$, 9%). Anal. Calcd for $C_{24}H_{21}N_3S$: C 75.16, H 5.52, N 10.96; Found: C 75.10, H 6.15, N 10.93%.

1-Benzyl-3-ethyl-2-*N*-phenylthiocarbamoyl imidazolium inner salt (10f). 80%, mp 160–161 °C; ν_{max}/cm^{-1} 3131, 1589, 1529 and 1500; δ_H ($CDCl_3$) 7.51 (d, *J* 6.1 Hz, 2H, Ph-H), 7.40–7.46 (m, 7H, Ph-H), 7.12 (t, *J* 7.1 Hz, 1H, Ph-H), 6.93 (s, 1H, imidazolinyl-H), 6.76 (s, 1H, imidazolinyl-H), 5.51 (s, 2H, NC*H*$_2$Ph), 4.42 (q, *J* 7.3 Hz, 2H, NC*H*$_2$ CH$_3$), 1.61 (t, *J* 7.3 Hz, 3H, NCH$_2$C*H*$_3$); δ_C ($CDCl_3$) 166.3, 150.9, 147.0, 133.4, 129.3, 129.24, 129.19, 128.4, 123.6, 122.2, 118.2, 118.0, 51.9, 44.0, 15.1; EI-MS *m*/*z* 185 (100), 321 (M$^+$, 80), 322 (M + 1, 35%). Anal. Calcd for $C_{19}H_{19}N_3S$: C 70.99, H 5.96, N 13.07; Found: C 70.94, H 6.15, N 13.00%.

1-Benzyl-3-isopropyl-2-*N*-phenylthiocarbamoyl imidazolium inner salt (10g). 73%, mp 143–144 °C; ν_{max}/cm^{-1} 3120, 1592, 1523 and 1491; δ_H ($CDCl_3$) 7.51 (d, *J* 5.5, 2H, Ph-H), 7.38–7.43 (m, 7H, Ph-H), 7.10 (t, *J* 7.0, 1H, Ph-H), 6.97 (d, *J* 2.0, 1H, imidazolinyl-H), 6.74 (d, *J* 1.9, 1H, imidazolinyl-H), 5.47 (s, 2H, NC*H*$_2$Ph), 5.26 (m, 1H, NC*H*$(CH_3)_2$), 1.59 (d, *J* 6.7, 6H, NCH(C*H*$_3$)$_2$); δ_C ($CDCl_3$) 166.6, 151.0, 146.9, 133.3, 129.4, 129.3, 129.2, 128.6, 123.6, 122.2, 118.3, 114.7, 51.8, 51.0, 22.8; EI-MS *m*/*z* 134 (100), 335 (M$^+$, 67), 336 (M + 1, 30%). Anal. Calcd for $C_{20}H_{21}N_3S$: C 71.61, H 6.31, N 12.53; Found: C 71.64, H 6.70, N 12.48%.

1-Benzyl-3-butyl-2-*N*-phenylthiocarbamoyl imidazolium inner salt (10h). 89%, mp 165–166 °C; ν_{max}/cm^{-1} 3116, 1594, 1575, 1526 and 1495; δ_H ($CDCl_3$) 7.51 (d, *J* 5.6, 2H, Ph-H), 7.41 (br s, 7H, Ph-H), 7.11 (br s, 1H, Ph-H), 6.89 (d, *J* 1.7, 1H, imidazolinyl-H), 6.74 (d, *J* 1.7, 1H, imidazolinyl-H), 5.52 (s, 2H, NC*H*$_2$Ph), 4.36 (t, *J* 7.6, 2H, N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 1.98 (quintet, *J* 7.5, 2H, N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.47 (sextet, *J* 7.5, 2H, N-CH$_2$CH$_2$C*H*$_2$CH$_3$), 1.00 (t, *J* 7.3, 3H, N-CH$_2$CH$_2$CH$_2$C*H*$_3$); δ_C ($CDCl_3$) 166.4, 151.0, 147.1, 133.4, 129.30, 129.25, 129.2, 128.6, 123.6, 122.1, 118.6, 118.1, 52.0, 48.7, 31.8, 19.8, 13.6; EI-MS *m*/*z* 135 (100), 349 (M$^+$, 68), 350 (M + 1, 25%). Anal. Calcd for $C_{21}H_{23}N_3S$: C 72.17, H 6.63, N 12.02; Found: C 72.01, H 6.94, N 12.05%.

2. General procedure for the reaction of 2-phenylthiocarbamoyl imidazolium inner salts 10 with dimethyl acetylenedicarboxylate (DMAD)

At 20–30 °C, the solution of DMAD (1 mmol) in THF (10 cm^3) was added dropwise to the yellow solution of the imidazolium inner salt **10** (1 mmol) in THF (20 cm^3). The reaction mixture was stirred at 20–30 °C for half a hour. After removal of the solvent, the products **11** were isolated by chromatography on silica gel eluting with a mixture of petroleum ether (30–60 °C) and ethyl acetate (5 : 1).

Dimethyl 2-(*N*,*N*′-diethylimidazolin-2-ylidene)-3-thioxobutanedioate (11a). 69%, mp 187–189 °C; ν_{max}/cm^{-1} 3098, 3055, 1722, 1691, 1503, 1464, 1442 and 1429; δ_H ($CDCl_3$) 7.22 (s, 2H, imidazolinyl-H), 4.07 (q, *J* 7.4, 4H, 2 × NC*H*$_2$CH$_3$), 3.93 (s, 3H, OC*H*$_3$), 3.67 (s, 3H, OC*H*$_3$), 1.50 (t, *J* 7.4, 6H, 2 × NCH$_2$C*H*$_3$); δ_C ($CDCl_3$) 191.8, 170.3, 163.2, 146.3, 119.4, 99.4, 52.5, 51.4, 43.5, 15.0; ESI-MS *m*/*z* 299 (M + 1). Anal. Calcd for $C_{13}H_{18}N_2O_4S$: C 52.33, H 6.08, N 9.39; Found: C 52.11, H 6.18, N 9.31%.

Dimethyl 2-[*N*,*N*′-di(isopropyl)imidazolin-2-ylidene]-3-thioxobutanedioate (11b). 62%, mp 197–198 °C; ν_{max}/cm^{-1} 3178, 1729, 1689, 1573, 1503, 1475 and 1447; δ_H ($CDCl_3$) 7.26 (s, 2H, imidazolinyl-H), 4.55–4.60 (m, 2H, 2 × NC*H*$(CH_3)_2$), 3.94 (s, 3H, OC*H*$_3$), 3.65 (s, 3H, OC*H*$_3$), 1.57 (d, *J* 6.6 Hz, 6H, NCH(C*H*$_3$)$_2$), 1.42 (d, *J* 6.6 Hz, 6H, NCH(C*H*$_3$)$_2$); δ_C ($CDCl_3$) 192.1, 170.5, 163.2, 144.7, 117.1, 99.4, 52.5, 51.2, 50.8, 23.2, 23.0; ESI-MS *m*/*z* 327 (M + 1). Anal. Calcd for $C_{15}H_{22}N_2O_4S$: C 55.20, H 6.79, N 8.58; Found: C 55.34, H 6.97, N 8.64%.

Dimethyl 2-(*N*,*N*′-dibutylimidazolin-2-ylidene)-3-thioxobutanedioate (11c). 71%, mp 130–131 °C; ν_{max}/cm^{-1} 3126, 1725, 1680, 1576, 1501 and 1443; δ_H ($CDCl_3$) 7.18 (s, 2H, imidazolinyl-H), 3.94–4.03 (m, 4H, 2 × N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 3.92 (s, 3H, OC*H*$_3$), 3.65 (s, 3H, OC*H*$_3$), 1.81 (sextet, *J* 7.1, 4H, 2 × N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.37 (sextet, *J* 7.3, 4H, 2 × N-CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.95 (t, *J* 7.3, 6H, 2 × N-CH$_2$CH$_2$CH$_2$C*H*$_3$); δ_C ($CDCl_3$) 191.7, 170.4, 163.3, 146.5, 120.0, 99.5, 52.5, 51.2, 48.3, 31.4, 19.6, 13.5; ESI-MS *m*/*z* 355 (M + 1). Anal. Calcd for $C_{17}H_{26}N_2O_4S$: C 57.60, H 7.39, N 7.90; Found: C 57.66, H 7.48, N 7.94%.

Dimethyl 2-[*N*-butyl-*N*′-isopropylimidazolin-2-ylidene]-3-thioxobutanedioate (11d). 74%, mp 144–145 °C; ν_{max}/cm^{-1} 3160, 3135, 1726, 1684, 1570, 1501, 1483, 1460 and 1428; δ_H ($CDCl_3$) 7.23 (d, *J* 2.0, 1H, imidazolinyl-H), 7.21 (d, *J* 1.9, 1H, imidazolinyl-H), 4.53–4.59 (m, 1H, NC*H*(CH_3)), 3.94–4.05 (m, 2H, N-C*H*$_2$CH$_2$CH$_2$CH$_3$), 3.93 (s, 3H, OC*H*$_3$), 3.65 (s, 3H, OC*H*$_3$), 1.78–1.84 (m, 2H, N-CH$_2$C*H*$_2$CH$_2$CH$_3$), 1.55 (d, *J* 6.7, 3H, NCH(C*H*$_3$)), 1.42 (d, *J* 6.7, 3H, NCH(C*H*$_3$)), 1.35–1.40 (m, 2H, N-CH$_2$CH$_2$C*H*$_2$CH$_3$), 0.95 (t, *J* 7.4, 3H, N-CH$_2$CH$_2$CH$_2$C*H*$_3$); δ_C ($CDCl_3$) 191.9, 170.4, 163.3, 145.6, 120.6, 116.5, 99.5, 52.5, 51.2, 51.0, 48.1, 31.5, 23.3, 22.9, 19.6, 13.5; ESI-MS *m*/*z* 341 (M + 1). Anal. Calcd for $C_{16}H_{24}N_2O_4S$: C 56.45, H 7.11, N 8.22; Found: C 56.39, H 7.13, N 8.19%.

Dimethyl 2-(*N*,*N*′-dibenzylimidazolin-2-ylidene)-3-thioxobutanedioate (11e). 60%, mp 167–168 °C; ν_{max}/cm^{-1} 3138, 1729, 1685, 1577, 1497 and 1452; δ_H ($CDCl_3$) 7.38–7.39 (m, 6H, Ph-H), 7.34–7.36 (m, 4H, Ph-H), 6.95 (s, 2H, imidazolinyl-H), 5.16 (d, *J* 14.7, 2H, 2 × N-C*H*$_A$H$_B$), 5.12 (d, *J* 14.7, 2H, 2 × N-CH$_A$*H*$_B$), 3.94 (s, 3H, OC*H*$_3$), 3.51 (s, 3H, OC*H*$_3$); δ_C ($CDCl_3$) 191.5, 170.3, 163.1,

147.0, 133.1, 129.2, 129.1, 129.0, 120.2, 99.7, 52.5, 52.2, 51.2; ESI-MS m/z 423 (M + 1). Anal. Calcd for $C_{23}H_{22}N_2O_4S$: C 65.39, H 5.25, N 6.63; Found: C 65.27, H 5.59, N 6.58%.

Dimethyl 2-[*N*-benzyl-*N*′-ethylimidazolin-2-ylidene]-3-thioxobutanedioate (11f). 78%, mp 166–167 °C; ν_{max}/cm^{-1} 3125, 1718, 1693, 1492, 1458 and 1440; δ_H ($CDCl_3$) 7.38–7.40 (m, 3H, Ph-H), 7.34–7.36 (m, 2H, Ph-H), 7.18 (s, 1H, imidazolinyl-H), 7.10 (s, 1H, imidazolinyl-H), 5.16 (d, J 15.5, 1H, N-CH_AH$_B$), 5.13 (d, J 15.4, 1H, N-CH$_A$$H_B$), 4.05–4.10 (m, 2H, NC$H_2CH_3$), 3.94 (s, 3H, OC$H_3$), 3.58 (s, 3H, OC$H_3$), 1.49 (t, J 7.4, 3H, NCH$_2$CH_3); δ_C ($CDCl_3$) 191.5, 170.4, 163.1, 146.5, 133.2, 129.2, 129.1, 129.0, 120.3, 119.6, 99.6, 52.5, 52.1, 51.2, 43.7, 15.0; ESI-MS m/z 361 (M + 1). Anal. Calcd for $C_{18}H_{20}N_2O_4S$: C 59.98, H 5.59, N 7.77; Found: C 59.93, H 5.72, N 7.76%.

Dimethyl 2-[*N*-benzyl-*N*′-isopropylimidazolin-2-ylidene]-3-thioxobutanedioate (11g). 61%, mp 162–163 °C; ν_{max}/cm^{-1} 3100, 1723, 1690, 1574, 1488 and 1457; δ_H ($CDCl_3$) 7.37–7.40 (m, 3H, Ph-H), 7.34–7.36 (m, 2H, Ph-H), 7.20 (d, J 2.0, 1H, imidazolinyl-H), 7.03 (d, J 1.8, 1H, imidazolinyl-H), 5.14 (s, 2H, NCH_2Ph), 4.55–4.60 (m, 1H, NCH(CH$_3$)), 3.94 (s, 3H, OCH_3), 3.56 (s, 3H, OCH_3), 1.55 (d, J 6.7, 3H, NCH(CH_3)), 1.43 (d, J 6.7, 3H, NCH(CH_3)); δ_C ($CDCl_3$) 191.6, 170.4, 163.1, 145.8, 133.3, 129.2, 129.1, 129.0, 120.7, 116.6, 99.7, 52.5, 52.0, 51.2, 23.4, 22.7; ESI-MS m/z 375 (M + 1). Anal. Calcd for $C_{19}H_{22}N_2O_4S$: C 60.94, H 5.92, N 7.48; Found: C 61.05, H 6.28, N 7.43%.

Dimethyl 2-[*N*-benzyl-*N*′-butylimidazolin-2-ylidene]-3-thioxobutanedioate (11h). 73%, mp 113–114 °C; ν_{max}/cm^{-1} 3130, 3109, 1715, 1693, 1577, 1503, 1466 and 1437; δ_H ($CDCl_3$) 7.38–7.39 (m, 3H, Ph-H), 7.34 (d, J 7.4 Hz, 2H, Ph-H), 7.15 (s, 1H, imidazolinyl-H), 6.99 (s, 1H, imidazolinyl-H), 5.15 (d, J 15.0 Hz, 1H, N-CH_AH$_B$), 5.12 (d, J 15.0 Hz, 1H, N-CH$_A$$H_B$), 3.99 (t, J 6.2 Hz, 2H, N-CH_2CH$_2$CH$_2$CH$_3$), 3.93 (s, 3H, OCH_3), 3.57 (s, 3H, OCH_3), 1.79–1.86 (m, 2H, N-CH$_2$CH_2CH$_2$CH$_3$), 1.37 (quintet, J 7.4 Hz, 2H, N-CH$_2$CH$_2$CH_2CH$_3$), 0.95 (t, J 7.3 Hz, 3H, N-CH$_2$CH$_2$CH$_2$CH_3); δ_C ($CDCl_3$) 191.6, 170.4, 163.1, 146.7, 133.3, 129.2, 129.1, 129.0, 120.1, 99.6, 52.5, 52.2, 51.2, 48.4, 31.4, 19.6, 13.5; ESI-MS m/z 389 (M + 1). Anal. Calcd for $C_{20}H_{24}N_2O_4S$: C 61.84, H 6.23, N 7.21. Found: C 61.87, H 6.35, N 7.27%.

Acknowledgements

This work was supported by the National Natural Science Foundation of China for Distinguished Young Scholars (No. 20525207), National Natural Science Foundation of China (20672013), Program for New Century Excellent Talents in University (No. NCET-04-0143).

References

1 Review: R. A. Bunce, *Tetrahedron*, 1995, **51**, 13103; P. J. Parsons, C. S. Penkett and A. J. Shell, *Chem. Rev.*, 1996, **96**, 195.
2 K. C. Nicolaou, W. E. Barnette and P. Ma, *J. Org. Chem.*, 1980, **45**, 1463; K. C. Nicolaou and W. E. Barnette, *J. Chem. Soc., Chem. Commun.*, 1979, 1119.
3 S. F. Martin, C. Tu, M. Kimura and S. H. Simonsen, *J. Org. Chem.*, 1982, **47**, 3634.
4 J. D. Winkler, S. Kim, K. R. Condroski, A. Asensio and K. N. Houk, *J. Org. Chem.*, 1994, **59**, 6879; T.-S. Chou, H.-H. Tso and L.-J. Chang, *J. Chem. Soc., Chem. Commun.*, 1985, 236; K. Ando, M. Kankake, T. Suzuki and H. Takayama, *Synlett*, 1994, 741.
5 Z.-Q. Yuan, H. Ishikawa and D. L Boger, *Org. Lett.*, 2005, **7**, 741; G. I. Elliott, J. Velcicky, H. Ishikawa, Y.-K. Li and D. L. Boger, *Angew. Chem., Int. Ed.*, 2006, **45**, 620.
6 H.-J. Schönherr and H.-W. Wanzlick, *Chem. Ber.*, 1970, **103**, 1037; H. E. Winberg and D. D. Coffman, *J. Am. Chem. Soc.*, 1965, **87**, 2776; M. Regitz, J. Hocker, W. Schössler, B. Weber and A. Liedhegener, *Justus Liebigs Ann. Chem.*, 1971, **748**, 1; B. Cetinkaya, E. Cetinkaya, J. A. Chamizo, P. B. Hitchcock, H. A. Jasim, H. Kücükbay and M. F. Lappert, *J. Chem. Soc., Perkin Trans. 1*, 1998, 2047.
7 M. Regitz and J. Hocker, *Synthesis*, 1970, 301; R. W. Hoffmann, B. Hagenbruch and D. M. Smith, *Chem. Ber.*, 1977, **110**, 23; A. Sudo, K. Igarashi and T. Endo, *J. Polym. Sci., Part A: Gen. Pap.*, 2000, **38**, 4200.
8 M.-F. Liu, B. Wang and Y. Cheng, *Chem. Commun.*, 2006, 1215; Y. Cheng, M.-F. Liu, D.-C. Fang and X.-M. Lei, *Chem.–Eur. J.*, 2007, Early View, Published Online: 26 Feb, DOI: 10.1002/chem.200601482.
9 Crystal data for **11g**: $C_{19}H_{22}N_2O_4S$, M = 374.45, T = 294 K, orthorhombic, space group $P2(1)2(1)2(1)$, a = 9.416(2), b = 13.560(3), c = 15.727(3) Å, α = 90°, β = 90°, γ = 90°, V = 2008.1(8) Å^3, Z = 4, ρ_{calcd} = 1.239 g cm^{-3}, absorption coefficient 0.186 mm^{-1}, reflections collected/unique 10459/3551 [R(int) = 0.0397], final R indices [$I > 2\sigma(I)$] R_1 = 0.0358, wR_2 = 0.0780. Because Friedel reflections were merged before the final refinement, no significance can be put on the refined Flack value [−0.02(8)]. CCDC reference number 638651. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b701326d.
10 K. Ando, M. Kankake, T. Suzuki and H. Takayama, *Synlett*, 1994, 741; Y. Gaoni, *Tetrahedron Lett.*, 1978, 3277; Y. Gaoni, *Tetrahedron Lett.*, 1977, 947; T. S. Chou, C. W. Ko and T. K. Yang, *Tetrahedron*, 1992, **48**, 8963.
11 D. M. Lemal and S. D. McGregor, *J. Am. Chem. Soc.*, 1966, **88**, 1335; M. J. S. Dewar and L. Chantranupong, *J. Am. Chem. Soc.*, 1983, **105**, 7161.
12 T. Sano, Y. Horiguchi and Y. Tsuda, *Heterocycles*, 1981, **16**, 889; B. A. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup and M. E. Brennan, *J. Am. Chem. Soc.*, 1967, **89**, 5964.
13 V. A. Roberts and M. E. Garst, *J. Org. Chem.*, 1985, **50**, 893.
14 H. Meier, *Angew. Chem., Int. Ed.*, 2005, **44**, 2482; E. Kleinpeter, *J. Serb. Chem. Soc.*, 2006, **71**, 1.
15 A. Forni and R. Destro, *Chem.–Eur. J.*, 2003, **9**, 5528; R. Benassi, C. Bertarini, E. Kleinpeter, F. Taddei and S. Thomas, *J. Mol. Struct. (THEOCHEM)*, 2000, **498**, 201; R. Benassi, C. Bertarini, L. Hilfert, G. Kempter, E. Kleinpeter, J. Spindler, F. Taddei and S. Thomas, *J. Mol. Struct.*, 2000, **520**, 273; E. Kleinpeter and A. Schulenburg, *Tetrahedron Lett.*, 2005, **46**, 5995.
16 E. Kleinpeter, S. Klod and W.-D. Rudorf, *J. Org. Chem.*, 2004, **69**, 4317; G. Favini, A. Gamba and R. Todeschini, *J. Chem. Soc., Perkin Trans. 2*, 1985, 915; K. Mohanalingam, P. C. Ray and P. K. Das, *Synth. Met.*, 1996, **82**, 47; S. R. Marder, L. T. Cheng, B. G. Tiemann, A. C. Friedli, M. Blanchard-Desce, J. W. Perry and J. Skindhoej, *Science*, 1994, **263**, 511; K. Mohanalingam and P. K. Das, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys.*, 1992, **31**, 518.
17 E. Stankovic, S. Toma, B. R. Van, I. Asselberghs and A. Persoons, *J. Organomet. Chem.*, 2001, **637–639**, 426; Z. Yuan, N. J. Taylor, T. B. Marder, I. D. Williams, S. K. Kurtz and L. T. Cheng, *J. Chem. Soc., Chem. Commun.*, 1990, 1489; P. Zhu, P. Wang and C. Ye, *Chem. Phy. Lett.*, 1999, **311**, 306; P. Wilhelm and M. Neuenschwander, *Helv. Chim. Acta*, 1999, **82**, 338.
18 K. Kurata, H. Awaya, Y. Tominaga, Y. Matsuda and G. Kobayashi, *Bunseki Kiki*, 1977, **15**, 413; M.-X. Wang, J.-M. Liang and Z.-T. Huang, *J. Chem. Res. (S)*, 1994, 166; J. Sandstrom and I. Wennerbeck, *J. Chem. Soc. D*, 1971, 1088; R. Destro, U. Cosentino, G. Moro, E. Ortoleva and T. Pilati, *J. Mol. Struct.*, 1989, **212**, 97.

