An Unprecedented Synthesis of Eight-Membered-Ring Cyclic Thioimidic Esters by a Three-Component Reaction

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Abstract: The three-component reaction of the isocyanides and dialkyl acetylenedicarboxylates or dibenzoylacetylene (DBA) in the presence of elemental sulfur is described. The reaction afforded the corresponding eight-membered cyclic thioimidic esters in good yields.

Key words: three-component reaction, acetylenic compound, elemental sulfur, cyclic thioimidic ester, eight-membered ring

There has been a great interest in the sulfur containing compounds because of their potential biological activity and pharmaceutical significance.[1] On the other hand, organosulfur compounds are also versatile reagents in organic synthesis.[2] There are many methods available for the synthesis of such compounds,[3] among which a number of sulfur-transfer reagents have also been reported.[3,4]

Utilization of elemental sulfur is a challenging synthetic methodology for the preparation of organosulfur compounds. Conventional methods, however, in general require harsh conditions. It was considered that transition metal catalyzed activation of elemental sulfur could be an interesting approach to control sulfuration reaction.[5] The abundance of sulfur, its low cost, and its almost nonodorous nature is highly desirable in industrial or academic processes.[6] However, few such insertions involving elemental sulfur as the intervening species have been described.[7] We now wish to incorporate elemental sulfur in the area of isocyanide-based multicomponent reactions (IMCRs).

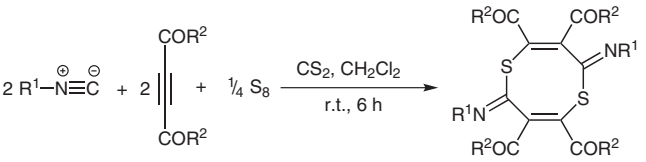
Isocyanide-based multicomponent reactions now occupy a position of importance in synthetic organic chemistry, mainly due to the contributions of Ugi and co-workers.[8,9] In addition to many variations of the classical Ugi four-component condensation (U-4CC), other IMCRs have entered the arena in recent years.[10] One such class, the reactivity of nucleophilic carbenes such as isocyanides toward dimethyl acetylenedicarboxylate (DMAD), is well documented.[11] The reaction of isocyanides with C≡C bonds occurs in a stepwise manner through a zwitterionic intermediate, the ultimate fate of which appears to be dictated by the nature of the original triple-bonded substrate.[12]

Although the trapping of the 1:1 intermediates formed between dialkyl acetylenedicarboxylates and isocyanides with O–H, N–H, and C–H acids has been widely studied,[13–17] trapping of the initially formed 1:1 intermediate with elemental sulfur has not been reported.

As part of our current studies[18–21] on the development of new routes to heterocyclic system we wish to report a simple one-pot three-component reaction between dialkyl acetylenedicarboxylates or dibenzoylacetylene and isocyanides in the presence of elemental sulfur to yield cyclic thioimidic esters. The thioimidates are useful intermediates,[22] and recently a preparation was reported that uses imidoyltriphenylphosphonium methylides.[23]

The reaction of alkyl isocyanides **1** with acetylenic esters **2** in the presence of elemental sulfur, proceeded spontaneously without activation of elemental sulfur at room temperature in anhydrous dichloromethane–carbon disulfide mixture (1:10) and was over within six hours to produce cyclic thioimidic esters **3** in 80–92% yields (Table 1).

Table 1 Reaction of Isocyanides **1** with Acetylenedicarboxylates **2** in the Presence of Elemental Sulfur



1 **2** **3**

Entry	R^1	R^2	Product	Yield (%)[a] of **3**
1	*t*-Bu	OMe	**3a**	90
2	*c*-Hex	OMe	**3b**	87
3	*t*-Bu	OEt	**3c**	85
4	*c*-Hex	OEt	**3d**	92
5	*t*-Bu	O*t*-Bu	**3e**	84
6	*c*-Hex	O*t*-Bu	**3f**	82
7	*t*-Bu	Ph	**3g**	80

[a] Isolated yield.

The structures of compounds **3a–g** were deduced from their elemental analyses, IR, and high-field ^{1}H and ^{13}C NMR spectra. The mass spectrum of **3a** displayed the molecular ion (M^+) peak at *m*/*z* 514, which is consistent with the tetramethyl 2,6-bis(*tert*-butylimino)-2*H*,6*H*-1,5-dithiocine-3,4,7,8-tetracarboxylate structure. The IR

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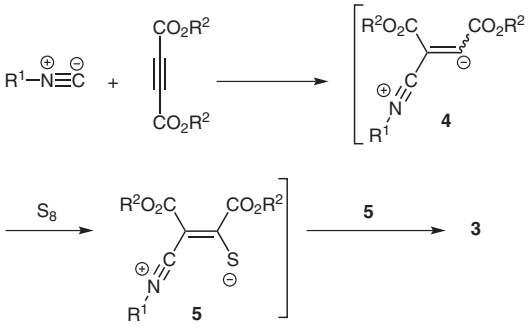
spectrum of **3a** exhibited absorption band due to the carbonyl groups of esters and imines at 1681 and 1638 cm^{-1}, respectively.

The ^1H NMR spectrum of **3a**, exhibited three sharp singlets readily recognized as arising from *tert*-butyl group (δ = 1.62), and two methoxy groups (δ = 3.65 and 4.51). The ^1H decoupled ^{13}C NMR spectrum of **3a** showed 9 distinct resonances in agreement with the tetramethyl 2,6-bis(*tert*-butylimino)-2*H*,6*H*-1,5-dithiocine-3,4,7,8-tetracarboxylate structure. The ^1H and ^{13}C NMR spectra of compounds **3b**–**g** are similar to those of **3a**, except for *N*-alkyl and the esters groups, which exhibit characteristic signals with appropriate chemical shifts (see experimental).

Although we have not established the mechanism of the reaction between the isocyanides and the acetylenic esters in the presence of the elemental sulfur in an experimental manner, a possible explanation is proposed in Scheme 1. On the basis of the well-established chemistry of isocyanides,[24] it is reasonable to assume that compounds **3** result from initial addition of alkyl isocyanides to the acetylenic esters and concomitant addition to elemental sulfur leading to charge transfer from negative carbon atom of zwitterions **4** onto sulfur atom that provide new zwitterions **5** and subsequent dimerization to produce cyclic thioimidic esters (Scheme 1).



Scheme 1 Plausible reaction mechanism for the generation of thioimidate derivatives from alkyl isocyanides **1** and acetylenic esters **2** in the presence of elemental sulfur

In summary, the present method carries the advantage that, not only is the reaction performed under neutral conditions, but also the substrates can be mixed without any activation or modification.

Dimethyl, diethyl, and di(*tert*-butyl) acetylenedicarboxylates, *tert*-butyl and cyclohexyl isocyanides were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. Dibenzoylacetylene was prepared according to the literature procedure.[11] Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on a Finnigan Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. ^1H and ^{13}C NMR spectra were recorded ($CDCl_3$ solution) on a Bruker DRX-500 Avance spectrometer at 500.1 and 125.8 MHz, respectively. IR spectra were recorded on a Shimadzu IR-460 spectrometer. Chromatography columns were prepared from Merck silica gel (230–240 mesh).

Tetramethyl 2,6-Bis(*tert*-butylimino)-2*H*,6*H*-1,5-dithiocine-3,4,7,8-tetracarboxylate (3a); Typical Procedure

To a magnetically stirred solution of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) and S_8 (0.512 g, 2 mmol) in anhyd CH_2Cl_2–CS_2 mixture (1:10, 10 mL) was added dropwise a solution of *tert*-butyl isocyanide (0.166 g, 2 mmol) in anhyd CH_2Cl_2 (2 mL) at 25 °C over 15 min. The reaction mixture was stirred for 6 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography over silica gel (Merck 230–240 mesh) using a hexane–EtOAc mixture (5:1) as eluent; yield: 0.46 g (90%); yellow powder; mp 95–97 °C.

IR (KBr): 1737 (C=O of ester), 1575 (C=N), 1689 (C=C), 1289 and 1248 cm^{-1} (C–O of ester).

^1H NMR (500.13 MHz, $CDCl_3$): δ = 1.91 (s, 18 H, 2 *t*-C_4H_9), 3.91 (s, 6 H, 2 CO_2CH_3), 3.96 (s, 6 H, 2 CO_2CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 27.67 [2 C(CH_3)$_3$], 53.39 (2 CO_2CH_3), 53.73 (2 CO_2CH_3), 65.90 (2 CMe_3), 138.57 (2 C=C), 140.42 (2 C=C), 159.18 (2 CO_2Me), 162.61 (2 CO_2Me), 183.56 (2 C=N).

MS: *m*/*z* (%) = 514 (M^+, 2), 484 (3), 234 (1), 168 (3), 101 (4), 58 (33), 43 (100).

Anal. Calcd for $C_{22}H_{30}N_2O_8S_2$ (514.60): C, 51.35; H, 5.88; N, 5.44. Found: C, 51.40; H, 5.80; N, 5.50.

Tetramethyl 2,6-Bis(cyclohexylimino)-2*H*,6*H*-1,5-dithiocine-3,4,7,8-tetracarboxylate (3b)

Yield: 0.50 g (87%); yellow powder; mp 125–127 °C.

IR (KBr): 1745 (C=O of ester), 1572 (C=N), 1689 (C=C), 1279 and 1247 cm^{-1} (C–O of ester).

^1H NMR (500.13 MHz, $CDCl_3$): δ = 1.01–2.29 (m, 20 H, 10 CH_2 of cyclohexyl), 3.84 (s, 6 H, 2 CO_2CH_3), 3.87 (s, 6 H, 2 CO_2CH_3), 4.93 (m, 2 H, 2 CH of cyclohexyl).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 24.94 (2 CH_2), 25.33 (4 CH_2), 32.66 (4 CH_2), 53.33 (2 CO_2CH_3), 53.80 (2 CO_2CH_3), 59.21 (2 NCH), 137.20 (2 C=C), 141.25 (2 C=C), 158.92 (2 CO_2Me), 162.49 (2 CO_2Me), 182.80 (2 C=N).

MS: *m*/*z* (%) = 566 (M^+, 2), 521 (22), 362 (27), 339 (6), 135 (5), 103 (10), 57 (30), 43 (100).

Anal. Calcd for $C_{26}H_{34}N_2O_8S_2$ (566.68): C, 55.11; H, 6.05; N, 4.94. Found: C, 55.10; H, 6.10; N, 4.85.

Tetraethyl 2,6-Bis(*tert*-butylimino)-2*H*,6*H*-1,5-dithiocine-3,4,7,8-tetracarboxylate (3c)

Yield: 0.48 g (85%); yellow powder; mp 105–107 °C.

IR (KBr): 1733 (C=O of ester), 1572 (C=N), 1689 (C=C), 1290 and 1242 cm^{-1} (C–O of ester).

^1H NMR (500.13 MHz, $CDCl_3$): δ = 1.34 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2 OCH_2CH_3), 1.40 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2 OCH_2CH_3), 1.90 (s, 18 H, 2 *t*-C_4H_9), 4.36 (q, $^3J_{H,H}$ = 7.1 Hz, 4 H, 2 OCH_2CH_3), 4.44 (q, $^3J_{H,H}$ = 7.1 Hz, 4 H, 2 OCH_2CH_3).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.98 and 14.08 (4 OCH_2CH_3), 27.71 [2 C(CH_3)$_3$], 62.53 and 63.26 (4 OCH_2CH_3), 65.76 (2 CMe_3), 138.95 (2 C=C), 140.29 (2 C=C), 158.85 (2 CO_2Et), 162.20 (2 CO_2Et), 183.72 (2 C=N).

MS: *m*/*z* (%) = 570 (M^+, 2), 386 (2), 317 (90), 272 (6), 215 (100), 187 (52), 145 (38), 84 (13), 57 (96).

Anal. Calcd for $C_{13}H_{19}NO_4S$ (570.71): C, 54.72; H, 6.71; N, 4.91. Found: C, 54.68; H, 6.80; N, 4.85.

Tetraethyl 2,6-Bis(cyclohexylimino)-2*H*,6*H*-1,5-dithiocine-3,4,7,8-tetracarboxylate (3d)
Yield: 0.58 g (92%); yellow powder; mp 120–122 °C.

IR (KBr): 1742 (C=O of ester), 1564 (C=N), 1688 (C=C), 1278 and 1247 cm^{-1} (C–O of ester).

^1H NMR (500.13 MHz, $CDCl_3$): δ= 1.15–2.21 (m, 20 H, 10 CH_2 of cyclohexyl), 1.32 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2 OCH_2CH_3), 1.37 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2 OCH_2CH_3), 4.35 (q, $^3J_{H,H}$ = 7.1 Hz, 4 H, 2 OCH_2CH_3), 4.42 (q, $^3J_{H,H}$ = 7.1 Hz, 4 H, 2 OCH_2CH_3), 5.00–5.03 (m, 2 H, 2 CH of cyclohexyl).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 13.95 and 14.04 (4 OCH_2CH_3), 25.06 (2 CH_2), 25.41 (4 CH_2), 32.78 (4 CH_2), 59.13 (2 NCH), 62.60 and 63.38 (4 OCH_2CH_3), 137.28 (2 C=C), 141.64 (2 C=C), 158.71 (2 CO_2Et), 162.15 (2 CO_2Et), 183.18 (2 C=N).

MS: *m*/*z* (%) = 622 (M^+, 2), 256 (30), 155 (62), 99 (78), 81 (56), 64 (100), 54 (58).

Anal. Calcd for $C_{30}H_{42}N_2O_8S_2$ (622.79): C, 57.86; H, 6.80; N, 4.56. Found: C, 57.80; H, 6.75; N, 4.45.

Tetra(*tert*-butyl) 2,6-Bis(*tert*-butylimino)-2*H*,6*H*-1,5-dithiocine-3,4,7,8-tetracarboxylate (3e)
Yield: 0.57 g (84%); yellow powder; mp 115–117 °C.

IR (KBr): 1729 (C=O of ester), 1574 (C=N), 1689 (C=C), 1289 and 1251 cm^{-1} (C–O of ester).

^1H NMR (500.13 MHz, $CDCl_3$): δ = 1.54 (s, 18 H, 2 CO_2t-C_4H_9), 1.62 (s, 18 H, 2 CO_2t-C_4H_9), 1.90 (s, 18 H, 2 *t*-C_4H_9).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 27.78 [2 $C(CH_3)_3$], 28.05 and 28.21 [2 $CO_2C(CH_3)_3$], 65.29 (2 CMe_3), 83.72 and 85.38 (2 CO_2CMe_3), 139.71 (2 C=C), 140.41 (2 C=C), 157.75 (2 CO_2CMe_3), 161.11 (2 CO_2CMe_3), 184.13 (2 C=N).

MS: *m*/*z* (%) = 682 (M^+, 2), 436 (3), 373 (6), 317 (2), 261 (4), 243 (3), 205 (24), 143 (4), 57 (100).

Anal. Calcd for $C_{34}H_{54}N_2O_8S_2$ (682.93): C, 59.80; H, 7.97; N, 4.10. Found: C, 59.70; H, 7.90; N, 4.00.

Tetra(*tert*-butyl) 2,6-Bis(cyclohexylimino)-2*H*,6*H*-1,5-dithiocine-3,4,7,8-tetracarboxylate (3f)
Yield: 0.60 g (82%); yellow powder; mp 110–112 °C.

IR (KBr): 1732 (C=O of ester), 1566 (C=N), 1688 (C=C), 1273 and 1249 cm^{-1} (C–O of ester).

^1H NMR (500.13 MHz, $CDCl_3$): δ = 1.10–2.15 (m, 20 H, 10 CH_2 of cyclohexyl), 1.53 (s, 18 H, 2 CO_2t-C_4H_9), 1.61 (s, 18 H, 2 CO_2t-C_4H_9), 5.00–5.04 (m, 2 H, 2 CH of cyclohexyl).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 25.04 (2 CH_2), 25.44 (4 CH_2), 28.02 and 28.20 [4 $CO_2C(CH_3)_3$], 32.81 (4 CH_2), 58.73 (2 NCH), 83.92 and 85.58 (4 CO_2CMe_3), 137.48 (2 C=C), 142.44 (2 C=C), 157.63 (2 CO_2CMe_3), 161.10 (2 CO_2CMe_3), 183.55 (2 C=N).

MS: *m*/*z* (%) = 735 (M^+, 2), 399 (3), 317 (6), 287 (8), 270 (5), 256 (92), 237 (14), 192 (13), 160 (13), 128 (32), 96 (23), 64 (100), 57 (74).

Anal. Calcd for $C_{38}H_{58}N_2O_8S_2$ (735.00): C, 62.10; H, 7.95; N, 3.81. Found: C, 62.00; H, 7.90; N, 3.75.

Phenyl[4,7,8-tribenzoyl-2,6-bis(*tert*-butylimino)-2*H*,6*H*-1,5-dithiocine-3-yl]methanone (3g)
Yield: 0.56 g (80%); yellow powder; mp 145–147 °C.

IR (KBr): 1664 (C=O), 1594 (C=N), 1650 cm^{-1} (C=C).

^1H NMR (500.13 MHz, $CDCl_3$): δ = 1.99 (s, 18 H, 2 *t*-C_4H_9), 7.34–7.76 (m, 20 H, 20 CH of 4 C_6H_5).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 27.96 [2 $C(CH_3)_3$], 65.89 (2 CMe_3), 128.57 (4 CH of C_6H_5), 128.81 (4 CH of C_6H_5), 129.03 (4 CH of C_6H_5), 129.57 (4 CH of C_6H_5), 133.64 (2 CH of C_6H_5), 134.43 (2 CH of C_6H_5), 136.00 (2 C_{ipso}), 136.42 (2 C_{ipso}), 144.33 (2 C=C), 146.46 (2 C=C), 184.35 (2 Ph*C*=O), 186.37 (2 Ph*C*=O), 190.05 (2 C=N).

MS: *m*/*z* (%) = 698 (M^+, 2), 365 (3), 302 (4), 285 (4), 279 (5), 265 (9), 217 (16), 167 (10), 105 (38), 77 (36), 57 (83), 43 (100).

Anal. Calcd for $C_{42}H_{38}N_2O_4S_2$ (698.89): C, 72.18; H, 5.48; N, 4.01. Found: C, 72.10; H, 5.40; N, 4.10.

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