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Nitroketene dithioacetal chemistry: Synthesis of 2-alkylthio-3-nitrothiophenes from nitroketene dithioacetate and chloromethyl ketones

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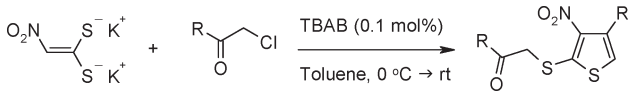

An effective synthesis of highly functionalized 3-nitrothiophenes was achieved from the reaction of simple, inexpensive, and readily available dipotassium 2-nitro-1,1-ethylyenedithiolate with α-chloromethyl ketones in toluene catalyzed by tetrabutylammonium bromide (TBAB). Thiophene formation is highly sensitive and selective for chlorine, present as a leaving group in α-chloromethyl ketones.

Nitroketene dithioacetals **2** are versatile two-carbon synthons, especially useful for the construction of heterocyclic compounds.[1] They can be assembled easily from inexpensive and readily available carbon disulfide, nitromethane, and alkylating agents in a two-step procedure.[2] The first step involves preparation of the dipotassium 2-nitro-1,1-ethylenedithiolate **1** from nitromethane, carbon disulfide, and potassium hydroxide. We have been investigating the products formed from the alkylation of dipotassium salt **1** with a variety of alkyl halides. We found that alkylation of salt **1** with simple alkyl halides in a mixture of ethanol−water furnished bis-alkylated products, viz., 1,1-di(2-alkylthio)-2-nitroethylenes **2** (route a, Scheme 1).[3] When the alkylation was carried out in acetonitrile with sterically hindered alkyl halides, the major products were 4-(2-alkylthio)-2-[(*Z*)-1-nitromethylidene]-1,3-dithioles **3**, formed by the reaction of two units of salt **1** with one unit of alkyl halide (route b).[4] Alkylation of **1** with propargyl bromide furnished 4-methylene-2-[1-nitromethylidene]-1,3-dithiolane **4** resulting from monoalkylation followed by cyclization (route c).[5] In continuation of these investigations, we considered reacting salt **1** with alkyl halides having an electrophilic carbonyl group in a 1,2-relationship, as found in acyl methyl chlorides. Previously, Jensen and co-workers have shown that alkylation of **1** with phenacyl bromide (2-bromo-1-phenyl-1-ethanone) led exclusively to bis-alkylated product **2** (R = CH_2COPh, Scheme 1) when the reaction was conducted in 1:1 aq MeOH.[6] We have reinvestigated the reaction and found that the bis-alkylation of **1** takes place exclusively even when conducted in different solvents like 1:2 aq MeOH, toluene with 1 mol % of tetrabutylammonium bromide (TBAB), or DMF. In complete contrast to the above result, we have discovered that the alkylation of **1** with phenacyl chloride (2-chloro-1-phenyl-1-ethanone) **6a** takes an unprecedented course (route d) to provide 3-nitrothiophene **5a** along with its precursor **7** (Scheme 1). Apparently, simple change of the leaving group from bromo to chloro in phenacyl halide resulted in alteration of the route to deliver the 3-nitrothiophene **5** instead of the bis-alkylated product **2**. We have investigated the scope of the transformation and report herein details of this study.

Thiophenes in general[7] and 3-nitrothiophenes[8] in particular have found numerous applications in pharmaceutical and technological fields. As an example, 3-nitro-2-thiophenethiol, a molecule having resemblance to the products of the present study, is a key building block in the synthesis of the calcium antagonist drug dilthiazem.[9] 2-Alkylthio-3-nitrothiophenes of the type **5** are useful precursors for further synthetic manipulation, as the alkylthio group can be replaced by nucleophiles. The reaction of nitrothiophenes with primary and secondary amines provides highly substituted butadienes through ring-opening pathways.[10]

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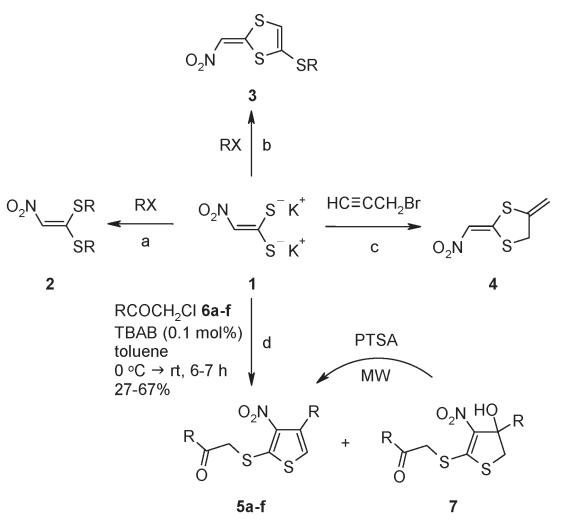
SCHEME 1. Reaction of Dipotassium Salt 1 with Different Alkyl Halides



5a, **6a**, **7**: R = Ph; **5b**, **6b**: R = Me; **5c**, **6c**: R = $C_6H_5SCH_2$; **5d**, **6d**: R = 4-$MeC_6H_4SCH_2$; **5e**, **6e**: R = 4-$ClC_6H_4SCH_2$; **5f**, **6f**: R = 4-$MeC_6H_4OCH_2$

Treatment of salt **1** with phenacyl chloride **6a** in toluene in the presence of tetrabutylammonium bromide (TBAB) as a phase transfer catalyst (PTC) provided 3-nitrothiophene **5a** (27%) and its precursor, the dihydrothiophene **7** (68%). There was no trace of bis-alkylated product **2** (R = CH_2COPh). The microwave-mediated dehydration of dihydrothiophene **7** with *p*-toluenesulfonic acid adsorbed over silica gel furnished a quantitative yield of **5a**. The structure of **5a** was determined by spectral (IR, ^1H NMR, ^{13}C NMR, 2D NMR, and MS) and analytical data. Characteristic singlets for C2H of the thiophene ring and SCH_2 appeared at δ 7.44 and 5.06 ppm, respectively. Supporting the assigned structure, the ^{13}C NMR spectrum displayed 14 lines with methylene carbon located at 43.5 ppm. We have conducted a competition reaction in which salt **1** was treated with 2 molar equiv each of phenacyl chloride **6a** and phenacyl bromide **8** to determine if 3-nitrothiophene product is formed in preference (Scheme 2). This reaction furnished bis-alkylated product **2a** as the major product in 77% yield. The thiophene **5a** (3%) and its precursor **7** (17%) were minor products. It became obvious from this experiment that phenacyl bromide is more reactive toward alkylation of **1** and the reaction takes route a (Scheme 1) to provide the bis-alkylated product.

The reaction of salt **1** with 1-chloroacetone **6b** furnished 1-[(4-methyl-3-nitrothiophen-2-yl)thio]propan-2-one **5b** exclusively and there was no trace of its precursor of type **7** (Scheme 1, Table 1). We have used this reaction as a test case to optimize conditions for 3-nitrothiophene formation. Initially, equivalents of 1-chloroacetone **6b** were varied from 0.5 to 2 to find out if the reaction takes a different course when there was change in the concentration of the alkylating agent. We found that there was no trace of 2:1 adduct of type **3** or 1:2 adduct of type **2** under these conditions. As anticipated from structure **5** the reaction required 2 equiv of **6b** for best yield of **5b**. The transformation worked well in nonpolar solvent (toluene, 67%) in the presence of PTC compared to polar aprotic solvent (DMF, 54%) or polar protic solvent (1:1 aq MeOH, 43%). It is to be noted that 1:1 aq methanol was found to be the best solvent for bis-alkylation to obtain nitroketene dithioacetals of type **2**.[3]

SCHEME 2. Competitive Reaction between Phenacyl Chloride 6a and Phenacyl Bromide 8 with the Salt 1

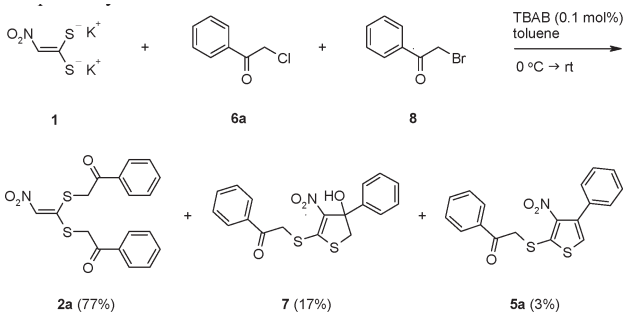
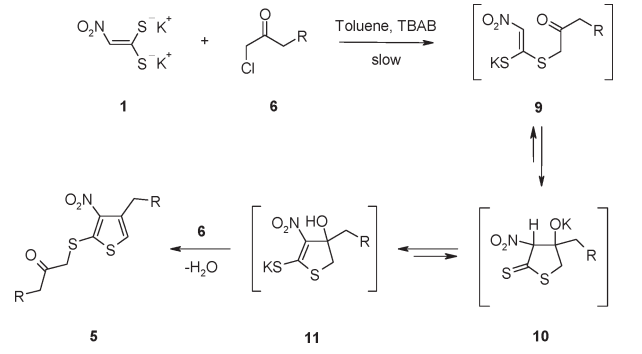


TABLE 1. Reaction of Dipotassium Salt 1 with α-Chloromethyl Ketones 6a−f

entry	compd	R	time, h	yield, %
1	**5a**	Ph	6	27[a]
2	**5b**	Me	4	67
3	**5c**	$C_6H_5SCH_2$	4	64
4	**5d**	4-$MeC_6H_4SCH_2$	6	56
5	**5e**	4-$ClC_6H_4SCH_2$	4	62
6	**5f**	4-$MeC_6H_4OCH_2$	4	36

[a]Dihydrothiophene **7** was obtained as major product in 68%.

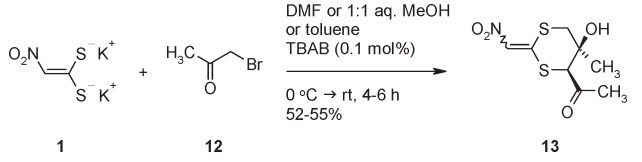
SCHEME 3. Mechanism for the Formation of 3-Nitrothiophenes 5



The transformation of salt **1** to 3-nitrothiophenes **5** proved to be general. We reacted salt **1** with different acylmethyl chlorides **6c−f** under optimized conditions and in all cases 3-nitrothiophenes **5c−f** were obtained exclusively (Table 1). Comparison of results from the reaction of salt **1** with phenacyl chloride **6a** and 1-chloro-3-(phenylthio)propan-2-one **6c** reveals that while in the first case dihydrothiophene **7** was the major product, in the later case 3-nitrothiophene **5c** was the exclusive product. This result indicates that antiperiplanar orientation for C4OH and C5H in **7** for dehydration is difficult to achieve.

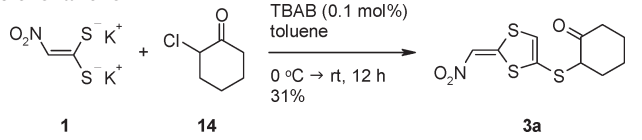
A possible mechanism for the 3-nitrothiophene **5** formation is given in Scheme 3. First alkylation of salt **1** with chloromethyl ketone **6** furnishes intermediate monoalkylated product **9**, which undergoes intramolecular nitroaldol condensation to provide **10** and **11**. Second alkylation of **11** followed by dehydration furnishes nitrothiophene **5**. Posteriori, we think that the second alkylation of the sulfanion in **9** with acyl alkyl chlorides is slow and therefore the intermediate has sufficient time to undergo nitro-aldol condensation. When alkylation was conducted with phenacyl bromide, first and second alkylations were fast to provide bis-alkylated products.

SCHEME 4. Reaction of Dipotassium Salt 1 with 1-Bromoacetone 12



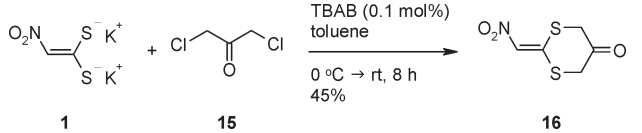
1 12 13

SCHEME 5. Reaction of Dipotassium Salt 1 with 2-Chlorocyclohexanone 14



1 14 3a

SCHEME 6. Reaction of Dipotassium Salt 1 with 1,3-Dichloroacetone 15



1 15 16

Indeed, this surmise was supported by the reaction between salt **1** and 1-bromoacetone **12** in solvents like toluene, DMF, or 1:1 aq MeOH (Scheme 4). In all the runs, this reaction furnished a diastereomeric mixture of 1-[(4*SR*,5*RS*)-5-hydroxy-5-methyl-2-(nitromethylidene)-1,3-dithian-4-yl]-ethanone **13** exclusively. The dithiane was formed by bis-alkylation followed by intramolecular aldol condensation.

Next, we reacted salt **1** with 2-chlorocyclohexanone **14** under optimized conditions. This reaction provided 1,3-dithiole, 2-{[2-(nitromethylidene)-1,3-dithiol-4-yl]thio}-cyclohexanone **3a** in modest yield (Scheme 5). This type **3** product (route b, Scheme 1) was formed by the reaction of 2 mol of salt with 1 mol of sterically demanding alkyl halide, namely, 2-chlorocyclohexanone **14**.

Finally, we reacted salt **1** with 1,3-dichloracetone **15** and this reaction provided 2-(nitromethylidene)-1,3-dithian-5-one **16** (Scheme 6) as the only product in moderate yield. This reaction obviously was going through the bis-alkylation mode to provide product of type **2** (route a, Scheme 1).

In conclusion, we have demonstrated an unprecedented facile two-step synthesis of 2-alkylthio-3-nitrothiophenes from simple and inexpensive starting materials like nitromethane, carbon disulfide, and acyl methyl chlorides. This reaction is selective to the leaving group (Br vs. Cl) and steric hindrance next to the acyl group. The trisubstituted thiophenes prepared in this study have high potential for further modification owing to the presence of diverse functional groups, viz., nitro, acyl, alkylthio, etc. We are presently exploring the reactions of the carbanion generated from the active methylene group next to the acyl group in **5** with 1,4-bifunctional reactants like 2-hydroxybenzaldehyde for generation of 2*H*-chromenols incorporating a 3-nitrothiophene unit.

Experimental Section

Representative Procedure: Preparation of 1-[(4-Methyl-3-nitrothiophen-2-yl)thio]propan-2-one, 5b: To a stirred suspension of freshly prepared dipotassium 2-nitro-1,1-ethylenedithiolate **1** (1 g, 4.71 mmol) in distilled toluene (10 mL) at 0 °C was added tetrabutylammonium bromide (TBAB; 0.1 mol %) in catalytic amount as a phase transfer catalyst. To this suspension was added a dilute solution of 1-chloroacetone **6b** (9.42 mmol) in distilled toluene (20 mL) by using a pressure equalizer funnel during 45 min. The resulting reaction mixture was then stirred vigorously at rt for 4 h. After the completion of the reaction (TLC; hexanes−EtOAc 8:2), the mixture was transferred into a beaker containing 20 g of crushed ice. The acidic (pH 5) reaction mixture was carefully neutralized with 0.1 N $NaHCO_3$ aqueous solution. The contents of the reaction mixture were separated into two phases on addition of dichloromethane (45 mL). The organic layer was washed with water (3 × 25 mL) and brine (2 × 15 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure resulted in the crude product as a dark brown pasty mass. The crude product was purified by column chromatography on silica gel with use of increasing amounts of EtOAc (5% to 40%) in hexanes as eluent. Evaporation of the pooled fractions furnished 0.80 g of **5b** in 67% yield as yellow crystals after recrystallization (CCl_4). Mp 124−126 °C (CCl_4); R_f 0.48 (hexanes−EtOAc 8:2); UV λ_{max} (MeOH) 373 (log ε = 4.08), 278 (log ε = 4.53), 252 (log ε = 4.62), 228 nm (log ε = 4.82); IR (KBr) ν_{max} 1710, 1544, 1485, 1355, 1315 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 6.80 (s, 1H), 3.91 (s, 2H), 2.47 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 200.8 (C), 146.7 (C), 142.6 (C), 135.4 (C), 118.8 (CH), 45.7 (CH_2), 28.6 (CH_3), 17.4 (CH_3); HRMS (ESI+) calcd for $C_8H_9NNaO_3S_2$ (MNa^+) 253.9922, found 253.9919. Anal. Calcd for $C_8H_9NO_3S_2$: C, 41.54; H, 3.92; N, 6.06; S, 27.73. Found: C, 41.51; H, 3.89; N, 6.05; S, 27.76.

2-[(3-Nitro-4-phenylthiophen-2-yl)thio]-1-phenylethanone, 5a: Following the representative procedure described above, the reaction of dipotassium 2-nitro-1,1-ethylenedithiolate **1** (1.50 g, 7.0 mmol) with phenacyl chloride **6a** (2.18 g, 14.1 mmol) in toluene (45 mL) and in the presence of a catalytic amount of TBAB (0.023 g, 0.1 mol %) at 0 °C for 1 h was stirred at rt for 6 h. The reaction provided **5a** and **7** after separation by column chromatography with use of increasing amounts of EtOAc (5% to 60%) in hexanes. Compound **5a** was obtained as a light yellow solid in 0.72 g (27%) yield. Mp 180−182 °C (50% hexanes−DCM); R_f 0.68 (hexanes−EtOAc 6:4); UV (MeOH) λ_{max} 411 (log ε = 3.66), 238 nm (log ε = 3.98); IR (KBr) ν_{max} 1679, 1623, 1492, 1319, 750, 688 cm^{-1}; ^1H NMR (400 MHz; DMSO-d_6) δ 8.07 (d, J = 7.6 Hz, 2H), 7.70 (t, J = 7.2 Hz, 1H), 7.57 (t, J = 7.6 Hz, 2H), 7.47 (s, 1H), 7.37−7.23 (m, 5H), 5.06 (s, 2H); ^{13}C NMR δ (100 MHz; DMSO-d_6) 193.6 (C), 148.2 (C), 141.4 (C), 138.0 (C), 135.6 (C), 134.7 (CH), 134.6 (C), 129.4 (2 × CH), 129.0 (2 × CH), 128.7 (2 × CH), 128.6 (2 × CH), 128.4 (CH), 123.7 (CH), 43.5 (CH_2); HRMS (ESI^+) calcd for $C_{18}H_{13}NNaO_3S_2$ (MNa^+) 378.0235, found 378. 0243. Anal. Calcd for $C_{18}H_{13}NO_3S_2$: C, 60.83; H, 3.69; N, 3.94; S, 18.04. Found: C, 60.79; H, 3.66; N, 3.88; S, 17.99.

2-[(4-Hydroxy-3-nitro-4-phenyl-4,5-dihydrothiophen-2-yl)thio]-1-phenylethanone, 7: Yield 1.7 g (68%), light yellow solid; mp 125−126 °C (MeOH); R_f:0.48 (hexanes−EtOAc 6:4); UV (MeOH) λ_{max} 372 (log ε = 4.60), 289 (log ε = 4.29), 244 nm (log ε = 4.71); IR (KBr) ν_{max} 3503, 1681, 1596, 1480, 1295, 752, 699 cm^{-1}; ^1H NMR (400 MHz; $CDCl_3$) δ 8.00 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.9 Hz, 2H), 7.30−7.43 (m, 4H), 4.64 (s, 2H), 4.26 (s, 1H), 3.79 (d, J = 11.9 Hz, 1H), 3.44 (d, J = 11.9 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 191.4 (C), 166.9 (C), 143.1 (C), 137.6 (C), 134.9 (C), 134.4 (CH), 129.1 (2 × CH), 129.0 (2 × CH), 128.5 (2 × CH), 128.4 (CH), 124.0 (2 × CH), 85.7 (C), 46.3 (CH_2), 41.8 (CH_2); HRMS (ESI^+) calcd for $C_{18}H_{15}NNaO_4S_2$ (MNa^+) 396.0340; found 396.0439. Anal. Calcd for $C_{18}H_{15}NO_4S_2$: C, 57.89; H, 4.05; N, 3.75; S, 17.17. Found: C, 57.88; H, 4.09; N, 3.71; S, 17.19.

2,2′-[(2-Nitroethene-1,1-diyl)dithiodiyl]bis(1-phenylethanone), 2a: Following the representative procedure, the reaction of dipotassium 2-nitro-1,1-ethylenedithiolate **1** (0.5 g, 2.35 mmol) with phenacyl bromide **8** (0.93 g, 4.69 mmol) in toluene (15 mL) and in the presence of TBAB (0.070 g, 0.1 mol %) as phase transfer catalyst at 0 °C for 4 h furnished 0.85 g of **2a** as a yellow solid in 96% yield. Mp 174−176 °C (MeOH); (lit. mp 173−174 °C); R_f 0.68 (hexanes−EtOAc 1:1); UV (MeOH) λ_{max} 362 nm (log ε = 3.6); IR (KBr) ν_{max} 1693, 1602, 1539, 1421, 1373, 806, 638 cm^{-1}; ^1H NMR (400 MHz; DMSO-d_6) δ 8.06 (d, J = 6.6 Hz, 4H), 7.72−7.54 (m, 7H), 5.13 (s, 2H), 5.05 (s, 2H); ^{13}C NMR (75 MHz; DMSO-d_6) δ 192.8 (C), 192.4 (C), 161.3 (C), 135.2 (C), 134.8 (CH), 134.2 (C), 134.0 (CH), 128.9 (2 × CH), 128.8 (2 × CH), 128.7 (2 × CH), 128.4 (2 × CH), 127.6 (CH), 43.3 (CH_2), 39.8 (CH_2); HRMS (ESI^+) calcd for $C_{18}H_{15}NNaO_4S_2$ (MNa^+) 396.0340, found 396.0337.

1-[(4*SR*,5*RS*)-5-Hydroxy-5-methyl-2-(nitromethylidene)-1,3-dithian-4-yl]ethanone, 13: Following the representative procedure, the reaction of dipotassium 2-nitro-1,1-ethylenedithiolate **1** (0.3 g, 1.41 mmol) with 1-bromoacetone **12** (0.39 g, 2.82 mmol) in toluene (10 mL) in the presence of TBAB (0.042 g, 0.1 mol %) as phase transfer catalyst at 0 °C for 4 h furnished 0.19 g of **13** as yellow solid in 55% yield. Mp 160−162 °C (MeOH); R_f 0.68 (hexanes−EtOAc 6:4); UV (MeOH) λ_{max} 361 (log ε = 2.7), 304 nm (log ε = 3.8); IR (KBr) ν_{max} 3439, 1703, 1520, 1438, 1310, 805, 680 cm^{-1}; ^1H NMR (400 MHz; DMSO-d_6) δ 7.49 (d, J = 5.6 Hz, 1H), 5.85 (s, 1H), 4.34 (d, J = 5.2 Hz, 1H), 2.98 (s, 2H), 2.31 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz; DMSO-d_6) δ 205.0 (C), 162.9 (C), 130.3 (CH), 75.4 (C), 65.8 (CH), 45.8 (CH_2), 31.7 (CH_3), 23.0 (CH_3); HRMS (ESI^+) calcd for $C_8H_{11}NNaO_4S_2$ (MNa^+) 272.0027, found 272.0018. Anal. Calcd for $C_8H_{11}NO_4S_2$: C 38.54; H, 4.45; N, 5.62; S, 25.72. Found: C 38.49; H, 4.43; N, 5.58; S, 25.68.

2-{[(2-(Nitromethylidene)-1,3-dithiol-4-yl]thio}cyclohexanone, 3a: Following the representative procedure, the reaction of dipotassium 2-nitro-1,1-ethylenedithiolate **1** (0.5 g, 2.35 mmol) with 2-chlorocyclohexanone **14** (0.62 g, 4.69 mmol) in toluene (15 mL) and in the presence of TBAB (0.077 g, 1 mol %) as phase transfer catalyst at 0 °C for 4 h furnished 0.212 g of **3a** as a yellow solid in 31% yield. Mp 178−180 °C (MeOH); R_f 0.68 (hexanes−EtOAc 6:4); UV (MeOH) λ_{max} 414 nm (log ε = 4.2); IR (KBr) ν_{max} 1718, 1521, 1468, 1377, 1289, 1241, 1203 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$/DMSO-d_6) δ 7.88 (s, 1H), 7.37 (s, 1H), 4.04 (t, 1H), 2.68−2.36 (m, 3H), 2.03−1.77 (m, 5H); ^{13}C NMR (75 MHz; $CDCl_3$ + DMSO-d_6) δ 205.3 (C), 166.8 (C), 129.8 (CH), 126.8 (CH), 120.9 (CH), 57.82 (CH), 40.3 (CH_2), 34.2 (CH_2), 23.7 (CH_2), 23.6 (CH_2); HRMS (ESI^+) calcd for $C_{10}H_{11}NNaO_3S_3$ (MNa^+) 311.9799, found 311.9791. Anal. Calcd for $C_{10}H_{11}NO_3S_3$: C, 41.50; H, 3.83; N, 4.84; S, 33.24. Found: C 41.51; H, 3.86; N, 4.83; S, 33.28.

2-(Nitromethylidene)-1,3-dithian-5-one, 16: Following the representative procedure, the reaction of dipotassium 2-nitro-1,1-ethylenedithiolate **1** (0.32 g, 1.5 mmol) with 1,3-dichloroacetone **15** (0.38 g, 3 mmol) in toluene (10 mL) and in the presence of TBAB (0.049 g, 0.1 mol %) as phase transfer catalyst at 0 °C for 4 h furnished 0.13 g of **16** as a yellow solid in 45% yield. Mp 81−82 °C (MeOH); R_f 0.68 (hexanes−EtOAc 4:6); UV (MeOH) λ_{max} 354 nm (log ε = 3.9); IR (KBr) ν_{max} 1720, 1622, 1515, 1434, 1398, 1265, 854, 677 cm^{-1}; ^1H NMR (300 MHz; $CDCl_3$) δ 7.72 (s, 1H), 2.24 (s, 2H), 2.10 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3 (C), 155.3 (C), 131.54 (CH), 39.30 (CH_2), 38.9 (CH_2); HRMS (ESI^+) calcd for $C_5H_5NNaO_3S_2$ (MNa^+) 213.9609, found 213.9607. Anal. Calcd for $C_5H_5NO_3S_2$: C 31.40; H, 2.64; N, 7.32; S, 33.54. Found: C, 31.38; H, 2.59; N, 7.29; S, 33.51.

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Supporting Information Available: General experimental methods, additional experimental procedures, compound characterization data, and copies of spectra. This material is available free of charge via the Internet at http://pubs.acs.org.