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Notes

New Synthesis of 1,3-Dithiole-2-thiones

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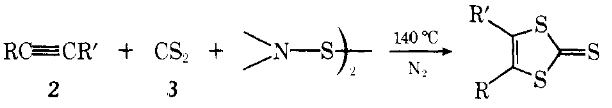
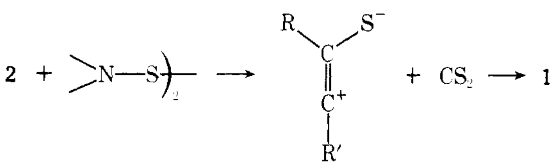
Tetrathiafulvalenes are important components in the formation of charge transfer complexes which have electrical conductance properties similar to those of metals.[1] These compounds are readily prepared[2] from 1,3-dithiole-2-thiones **1**. We now report a new one-step synthesis of **1** from substituted acetylenes **2**, carbon disulfide (**3**), and either bis(2,2,6,6-tetramethylpiperidine) disulfide or bis(morpholine) disulfide at 140 °C under nitrogen.



1

Previously we[3] reported that the reactions between **2** and bisamine disulfides led to the formation of thiophenes via the 1,3 dipoles derived from thioketocarbenes.[4] When the reaction of phenylacetylene and the piperidine disulfide was conducted in the presence of carbon disulfide, 4-phenyl-1,3-dithiole-2-thione was formed in 45% yield in addition to a 25% yield of a 3:1 mixture of 2,4- and 2,5-diphenylthiophenes (Table I). We propose[4] that the formation of the dithiole-2-thione arises from 1,3-dipolar cycloaddition between carbon disulfide and the thioketocarbene **4**.



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In the absence of carbon disulfide, *tert*-butylacetylene reacts with the piperidine disulfide to give sulfur but no thiophene, while in the presence of carbon disulfide 4-*tert*-butyl-1,3-dithiole-2-thione is formed in 41% yield. Thus, the thioketocarbene decomposes to sulfur and *tert*-butylacetylene faster than it undergoes cycloaddition to a second molecule of acetylene to form a thiophene, but it undergoes cycloaddition to carbon disulfide faster than it eliminates sulfur.

Ethyl phenylpropiolate, carbon disulfide, and morpholine disulfide react to give a 99% yield of 4-carboethoxy-5-phenyl-1,3-dithiole-2-thione. However, methyl 1,3-dithiole-2-thione-4-carboxylate and dimethyl 1,3-dithiole-2-thione-4,5-dicarboxylate, derived from methyl propiolate, carbon disulfide, and bis(morpholine) disulfide and from dimethyl acetylenedicarboxylate, carbon disulfide, and the piperidine disulfide, are accompanied by the tetrathiafulvalenes dimethyl [$\Delta^{2,2'}$-bi-1,3-dithiole]-4,4′-dicarboxylate in 10% yield and tetramethyl [$\Delta^{2,2'}$-bi-1,3-dithiole]-4,4′,5,5′-tetracarboxylate in 13% yield, respectively. The dithiole-2-thiones are easily separated from the bidithioles by elution column chromatography.

The formation of these tetrathiafulvalenes suggests an alternative dithiolium carbene mechanism for the reaction producing **1**. Electron-deficient acetylenes are known[5] to react with carbon disulfide to form nucleophilic 1,3-dithiolium carbenes which could undergo displacement at the sulfur in the bisamine disulfides to form an intermediate 1,3-dithiolium cation that collapses to **1**.

Diphenylacetylene failed to react with carbon disulfide and the piperidine disulfide. Since the acetylene does not react with carbon disulfide alone or with the amine disulfide alone to give either a thiophene or sulfur, this lack of reactivity for the acetylene supports neither mechanism more than the other.

However, since electron-rich acetylenes such as 2-butyne do not cycloadd to carbon disulfide and since the *tert*-butyldithiole-2-thione was formed from *tert*-butylacetylene, the thioketocarbene mechanism is more reasonable than the dithiolium carbene mechanism.

A comparison of this method of synthesis with those involving elemental sulfur and metal cation acetylides[6] shows that the latter is limited to monosubstituted acetylenes. The reaction between acetylenes and ethylene trithiocarbonate[11] is limited to electron-deficient acetylenes, while the reaction we report here is not limited in this way.

In conclusion, a simple one-step synthesis of 1,3-dithiole-2-thiones from substituted acetylenes, carbon disulfide, and bisamine disulfides has been demonstrated.

Experimental Section

All boiling points and melting points are uncorrected. IR spectra were obtained on a Perkin-Elmer Model 237 infrared spectrophotometer. NMR spectra were recorded on a Jeol-C-60H spectrometer with Me_4Si as an internal standard. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6 spectrometer with an ionizing potential of 70 eV. Microanalyses were done by Galbraith Laboratory, Inc. Phenylacetylene, ethyl phenylpropiolate, and dimethyl acetylenedicarboxylate were purchased from Aldrich Chemical Co., Inc., and methyl propiolate from Chemical Samples Co. Bis(morpholine) disulfide was bought from ICN Pharmaceuticals, Inc., and recrystallized from ethyl acetate before use. *tert*-Butylacetylene,[7] diphenylacetylene,[8] and bis(2,2,6,6-tetramethylpiperidine) disulfide[9] were prepared according to literature procedures.

General Procedure for the Synthesis of 1. Acetylene **2** and bisamine disulfide in a 4:1 molar ratio were dissolved in 75 mL of **3**, and the resulting solution was placed in a 2-L Parr bomb reactor

Table I. Yields of 1,3-Dithiole-2-thione (1)

RC≡CR′	Registry no.	$>$N—S$)_2$[a]	Registry no.	Yield of 1, %	Registry no.
PhC≡CH	536-74-3	A	14045-39-7	45	2314-61-6
$(CH_3)_3CC{\equiv}CH$	917-92-0	A		41	29507-67-3
$PhC{\equiv}CCO_2CH_2CH_3$	2216-94-6	B	103-34-4	99	65818-65-7
$HC{\equiv}CCO_2CH_3$	922-67-8	B		67	55526-01-7
$CH_3O_2CC{\equiv}CCO_2CH_3$	762-42-5	A		33	7396-41-0
PhC≡CPh	501-65-5	A		No reaction	

[a] A: bis(2,2,6,6-tetramethylpiperidine) disulfide. B: bis(morpholine) disulfide.

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equipped with a glass liner. The apparatus was flushed with N_2, sealed, and heated to 140 °C for 24 h. The pressure rose to 140 psi. After cooling, the apparatus was opened, the brown solution was transferred to a round-bottom flask, and the excess carbon disulfide was removed under vacuum. The dark residue was chromatographed over silica gel (30:1 weight ratio of silica gel to mixture) with benzene as eluent. The trithiones **1** are the first materials to elute followed in certain cases by the narrow dark bands corresponding to the tetrathiafulvalenes.

4-Phenyl-1,3-dithiole-2-thione. From 0.41 g (4.0 mmol) of phenylacetylene and 0.34 g (1.0 mmol) of bis(2,2,6,6-tetramethylpiperidine) disulfide, 0.19 g (45%) of trithione was obtained and recrystallized from ethanol: mp 117 °C (lit.[10] mp 117–118 °C); IR (KBr) 3100, 1485, 1445, 1055, 1045, 890, 740, 675 cm^{-1}; NMR (CS_2) δ 6.95 (1, s), 7.32 (5, s); mass spectrum, m/e (relative intensity) 210 (76), 134 (100), 121 (13), 102 (14), 91 (24), 90 (23), 77 (14).

4-*tert*-Butyl-1,3-dithiole-2-thione. From 0.33 g (4.0 mmol) of *tert*-butylacetylene and 0.40 g (1.0 mmol) of bis(2,2,6,6-tetramethylpiperidine) disulfide, 1.4 g (99%) of trithione was obtained and recrystallized from diethyl ether: mp 90 °C; IR (KBr) 2980, 1465, 1365, 1250, 1050, 1035, 898, 800, 655 cm^{-1}; NMR (CCl_4) δ 1.33 (9, s), 6.55 (1, s); mass spectrum, m/e (relative intensity) 190 (98), 175 (100), 113 (17), 70 (89), 69 (77), 58 (100).

Anal. Calcd for $C_7H_{10}S_3$: C, 44.21; H, 5.26; S, 50.52. Found: C, 44.11; H, 5.43; S, 50.18.

4-Carboethoxy-5-phenyl-1,3-dithiole-2-thione. From 3.48 g (20.0 mmol) of ethyl phenylpropiolate and 1.18 g (5.0 mmol) of bis(morpholine) disulfide, 1.4 g (99%) of trithione was obtained and recrystallized from diethyl ether: mp 92 °C; IR (KBr) 3000, 1740, 1540, 1450, 1260, 1205, 1090, 1080, 1025, 755, 690 cm^{-1}; NMR (CCl_4) δ 1.12 (3, t, J = 8.0 Hz), 4.10 (2, q, J = 8.0 Hz), 7.32 (5, s); mass spectrum, m/e (relative intensity) 282 (82), 178 (18), 166 (14), 145 (36), 134 (82), 133 (45), 121 (36), 89 (100), 77 (27).

Anal. Calcd for $C_{12}H_{10}O_2S_3$: C, 51.06; H, 3.54; S, 34.04. Found: C, 51.18; H, 3.64; S, 33.98.

Methyl 1,3-Dithiole-2-thione-4-carboxylate and 4,4′(5′)-Bis(carbomethoxy)-$\Delta^{2,2'}$-bi-1,3-dithiole. From 1.68 g (20.0 mmol) of methyl propiolate and 1.18 g (5.0 mmol) of bis(morpholine) disulfide, 0.63 g (67%) of trithione was obtained and recrystallized from benzene: mp 104 °C; IR (KBr) 3060, 1730, 1560, 1475, 1290, 1200, 1070, 1055, 735 cm^{-1}; NMR (CCl_4) δ 3.88 (3, s), 7.85 (1, s); mass spectrum, m/e (relative intensity) 192 (100), 161 (18), 134 (18), 133 (23), 116 (45), 76 (64), 64 (68), 57 (100), 45 (82).

Anal. Calcd for $C_7H_6O_4S_3$: C, 31.25; H, 2.08; S, 50.00. Found: C, 31.47; H, 2.15; S, 49.86.

In addition, 0.16 g (10%) of bidithiole was obtained and recrystallized from ligroin (70–90 °C): mp 240 °C (lit.[11] mp 244–245 °C); IR (KBr) 3080, 1722, 1440, 1250, 1200, 1160, 1050, 939, 829, 765, 730 cm^{-1}; mass spectrum, m/e (relative intensity) 320 (100), 204 (68), 161 (29), 105 (36), 101 (32), 76 (59).

Dimethyl 1,3-Dithiole-2-thione-4,5-dicarboxylate and Tetramethyl [$\Delta^{2,2'}$-Bi-1,3-dithiole]-4,4′,5,5′-tetracarboxylate. From 1.14 g (8.0 mmol) of dimethyl acetylenedicarboxylate and 0.69 g (2.0 mmol) of bis(2,2,6,6-tetramethylpiperidine) disulfide, 0.17 g (33%) of trithione was obtained and recrystallized from a mixture of toluene and hexane: mp 89 °C (lit.[11] mp 87 °C): IR (KBr) 1750, 1725, 1550, 1425, 1250, 1100, 1085, 1010, 920, 760 cm^{-1}; NMR (CCl_4) δ 3.86 (s); mass spectrum, m/e (relative intensity) 250 (100), 219 (22), 191 (22), 174 (26), 107 (48), 76 (49), 59 (96), 45 (28).

In addition, 0.11 g (13%) of bidithiole was obtained and recrystallized from methanol: mp 169–170 °C (lit.[5] mp 169–170 °C); IR (KBr) 1740, 1710, 1570, 1440, 1262, 1020 cm^{-1}; NMR (CCl_4) δ 3.85 (s); mass spectrum, m/e (relative intensity) 436 (100), 404 (11), 377 (30), 332 (22), 261 (50), 100 (17), 88 (44), 59 (55), 44 (44).

Registry No.—**3,** 75-15-0; 4,4′(5′)-bis(carbomethoxy)-$\Delta^{2,2'}$-bi-1,3-dithiole, 51751-18-9; tetramethyl [$\Delta^{2,2'}$-bi-1,3-dithiole]-4,4′,5,5′-tetracarboxylate, 26314-39-6.

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Phthalimido Phenylcarbamate: A New Isocyanate Generator

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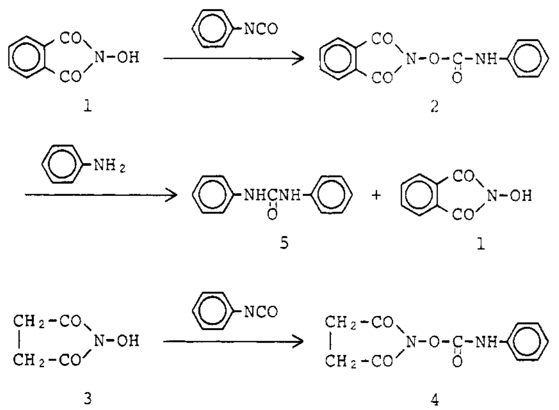
N-Hydroxyphthalimide (**1**) is an interesting compound as it has a unique acidic hydroxy group, and its alkylation[1–6] and esterification[7,8] have been reported in the literature. Regarding other reactions of **1**, however, very little has been published. As a result of our current interest in reactions of imide derivatives, we have recently examined the reaction of **1** with phenyl isocyanate. The reaction gives rise to the formation of a new type of urethane linkage which is expected to regenerate phenyl isocyanate on heating. The urethane compound would be a relatively stable solid which could be more easily handled with safety than the isocyanate, and moreover it could form a stable mixture with nucleophiles in solid state at ambient temperatures. These properties are especially useful in coating chemistry. We now wish to report the synthesis of phthalimido phenylcarbamate (**2**) and its potential as an isocyanate generator, comparing them with those of succinimido phenylcarbamate (**4**).



The carbamate **2** was prepared from *N*-hydroxyphthalimide (**1**) and phenyl isocyanate in dry dioxane or dimethylacetamide. The succinimide derivative **4** was synthesized from *N*-hydroxysuccinimide (**3**) similarly.

The thermal stability of **2** was examined by means of thermogravimetric analysis at a heating rate of 5 °C/min in air, and it was found that **2** decomposed with two-step weight loss. The first weight loss observed between 97 and 170 °C accounted for 45% of the initial weight, which was in good agreement with the theoretical value (42%) for the loss of phenyl isocyanate. The infrared spectrum of the solid obtained after the first weight loss was identical with that of the authentic **1.** Compound **2** was therefore thought to start regenerating phenyl isocyanate from around 100 °C in the solid state. Compound **4,** on the other hand, showed no two-step weight loss, probably on account of the volatility of the decomposed species. The weight loss started at 129 °C.

In order to evaluate its potential as an isocyanate generator, **2** was subjected to reaction with aniline at various temperatures. A dichloromethane solution containing equimolar amounts of **2** and aniline started to deposit diphenylurea (**5**) after about 4 h at room temperature (ca. 25 °C). Under these

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