Cycloaddition Reactions of 4,6-Diphenylthieno[3,4-*c*][1,2,5]oxadiazole and -[1,2,5]thiadiazole with Acetylenes[1]

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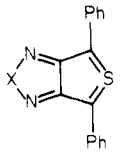
4,6-Diphenylthieno[3,4-*c*][1,2,5]oxadiazole containing tetravalent sulfur reacted with acetylenes to give the corresponding 1:2 adducts, *syn*-2-cyano-5-(3-isoxazolyl)-2,5-dihydrothiophene derivatives, accompanied by benzoxadiazoles. The reaction proceeds via initial formation of the cycloadducts of acetylenes across the thiocarbonyl ylide dipole. Subsequent ring cleavage of the oxadiazole ring of initial strained cycloadducts generates the nitrile oxide intermediates capable of undergoing cycloaddition to acetylenes to afford the 1:2 adducts, whereas desulfurization of the initial cycloadducts leads to the formation of benzoxadiazoles. On the other hand, analogous diphenylthieno[3,4-*c*][1,2,5]thiadiazole reacted with acetylenes to give the corresponding desulfurized benzothiadizoles in good yields.

Since tetraphenylthieno[3,4-*c*]thiophene was first prepared as an isolable nonclassical condensed thiophene,[2] syntheses of several stable, nonclassical 10π-electron condensed thiophenes have been reported. These compounds containing tetravalent sulfur are of considerable practical and theoretical interest.[3] Previously, we have reported on the preparation of 4,6-diphenylthieno[3,4-*c*][1,2,5]oxadiazole (**1**), containing tetravalent sulfur, and its cyclo-



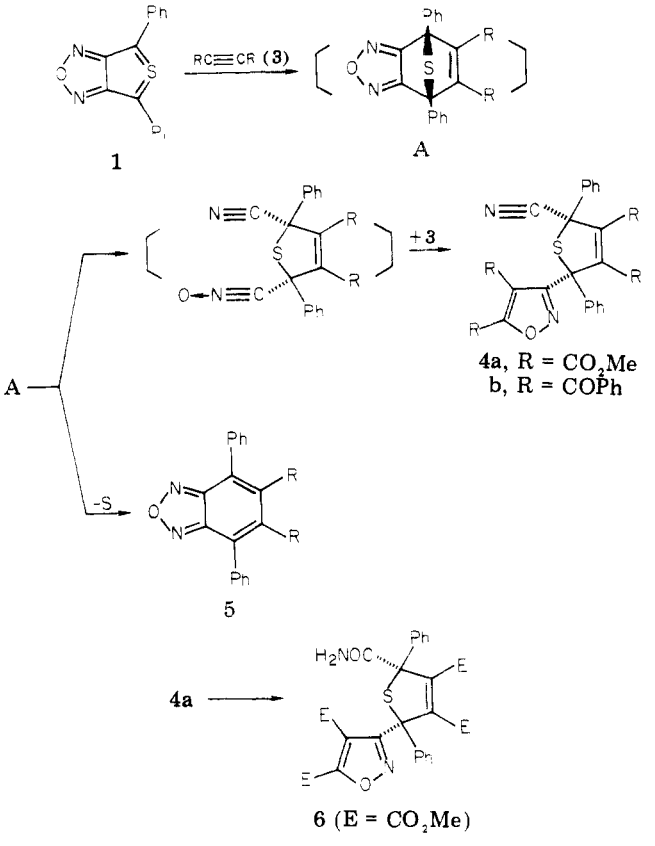
1, X = O
2, X = S

addition to olefins leading to strained oxadiazoles of the thianorbornane system.[4] It has also been found that both the endo and exo cycloadducts obtained from **1** and *N*-phenylmaleimide undergo thermal cleavage of the oxadiazole ring to nitrile and nitrile oxide moieties which can be captured as 1,3-cycloadducts by olefins and acetylenes,[5,6] whereas analogous cycloadducts formed from 4,6-diphenylthieno[3,4-*c*][1,2,5]thiadiazole (**2**) and the maleimide are subject to a retrocycloaddition reaction.[5]

In this regard, we have investigated the cycloaddition reactions of heterocycles **1** and **2** with acetylenes, expecting the formation of the highly strained cycloadducts, oxadiazoles and thiadiazoles, of the thianorbornene system.

Reaction of 4,6-Diphenylthieno[3,4-*c*][1,2,5]oxadiazole (1). When **1** was allowed to react with an equimolar amount of dimethyl acetylenedicarboxylate (**3a**) in refluxing benzene for 25.5 h, two products, **4a** and **5a**, were obtained in 27 and 2% yields, respectively, together with recovery of **1**. Although the structure of the major product **4a** will be described below, the molecular formula of **4a** agreed with that of a 1:2 adduct of **1** to **3a**. The minor product **5a** was assigned as 5,6-bis(methoxycarbonyl)-4,7-diphenylbenz[*c*][1,2,5]oxadiazole, arising from desulfurization of the expected 1:1 cycloadduct of **3a** across the thiocarbonyl ylide dipole of **1**. In the reaction employing 2 mol of **3a**, **4a** and **5a** were obtained in 54 and 4% yields, respectively.

Scheme I

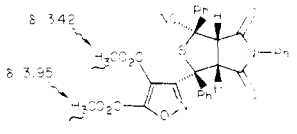


Similarly, **1** reacted with 2 mol of dibenzoylacetylene (**3b**) to give the corresponding 1:2 adduct **4b** and desulfurized benzoxadiazole **5b** in 66 and 5% yields, respectively. However, **1** did not react with diphenylacetylene even after 36 h in refluxing xylene. The pathways shown in Scheme I account for the formation of these products.

On the basis of spectral data as well as the mode of formation, the 1:2 adducts **4a** and **4b** were considered to be the *syn*-2-cyano-5-(3-isoxazolyl)-2,5-dihydrothiophene derivatives.[7] Although the IR spectrum of **4** showed a very

(1) Studies on 10π-Electron Heterocycles Containing Tetravalent Sulfur. Part 4. Part 3: ref 6.
(2) M. P. Cava and G. E. M. Husbands, *J. Am. Chem. Soc.*, **91**, 3952 (1969).
(3) M. P. Cava and M. V. Lakshmikantham, *Acc. Chem. Res.*, **8**, 139 (1975).
(4) O. Tsuge, T. Takata, and M. Noguchi, *Heterocycles*, **6**, 1173 (1977).
(5) O. Tsuge, T. Takata, and I. Ueda, *Chem. Lett.*, **1979**, 1029.
(6) O. Tsuge and T. Takata, *Heterocycles*, **14**, 423 (1980).

(7) By the X-ray diffraction study, the adduct of dimethyl acetylenedicarboxylate with the endo adduct formed from **1** and *N*-phenylmaleimide was conclusively determined to be the following structure (I. Ueda, T. Takata, and O. Tsuge, *Acta Crystallogr., Sect. B.*, in press).



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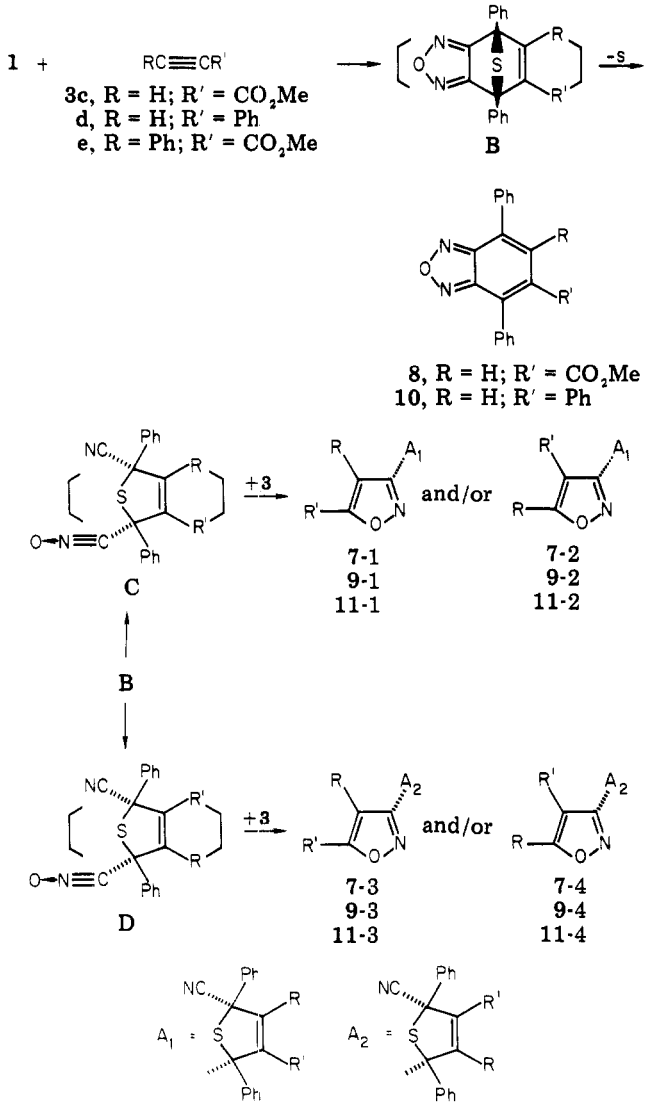
Scheme II

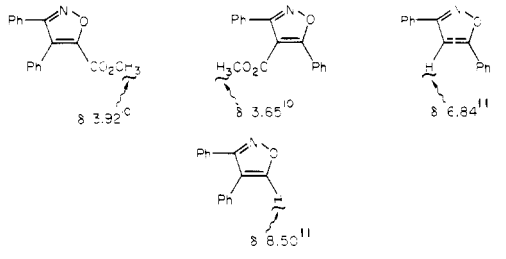


7, R = H; R' = CO_2Me; 9, R = H; R' = Ph; 11, R = Ph; R' = CO_2Me

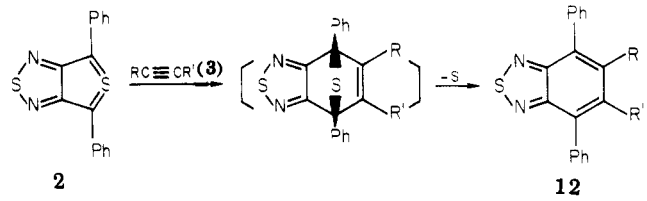
weak band ascribable to $\nu_{C\equiv N}$ absorption, the presence of the cyano group in **4** was confirmed by the conversion of **4a** to the carbamoyl derivative **6**. The ^{13}C NMR spectrum of **4a** supported strongly the assigned structure. The four singlets observed in the ^1H NMR spectrum of **4a** were assigned as the signals of the methoxycarbonyls (δ 3.61 and 3.64) on the dihydrothiophene moiety and of the 4- (δ 3.51) and 5-methoxycarbonyls (δ 3.89) on the isoxazole moiety, respectively.[7,8]

Next, the reaction of **1** with unsymmetrical acetylenes was investigated under similar conditions. In the reaction

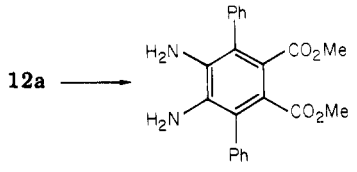
(8) The reported ^1H NMR spectral data of isoxazole derivatives are as follows.



Scheme III



a: R = R' = CO_2Me; b: R = R' = COPh; c: R = H, R' = CO_2Me; d: R = H, R' = Ph; e: R = Ph, R' = CO_2Me



of **1** with 2 mol of methyl propiolate (**3c**), a 36% yield of a mixture of isomeric 1:2 adducts **7** and a 31% yield of the desulfurized benzoxadiazole **8** were obtained, respectively. Now, four isomers, **7-1**, **7-2**, **7-3**, and **7-4**, are conceivable for the structures of **7**, because the generation of two isomeric nitrile oxides, C and D, is possible from the initial cycloadduct B as illustrated in Scheme II. However, attempts to isolate pure 1:2 adduct(s) were unsuccessful.

The ^1H NMR spectrum of the mixture of **7** exhibited signals at δ 3.51, 3.61, 3.64, 3.89, 9.0, and 9.05 (each s), besides signals in the region of aromatic protons. Both the signals at δ 9.0 and 9.05 can be readily assigned to the proton at the 5-position of the isoxazole ring.[8] On the basis of comparison of the ^1H NMR spectra of **4a** and reported isoxazole derivatives,[8] the signals at δ 3.61 and 3.64 were assigned to methoxycarbonyls on the dihydrothiophene moiety, and the signals at δ 3.51 and 3.89 were assigned to the 4- and 5-methoxycarbonyls of the isoxazole moiety. Thus, it was deduced that the mixture consisted of at least three isomers, **7-1** and/or **7-3**, **7-2**, and **7-4**. Also, the ratio of [**7-1** and/or **7-3**] to [**7-2** + **7-4**] in the mixture was estimated to be ca. 9:1 on the basis of the ^1H NMR spectrum.

Upon reaction with phenylacetylene (**3d**) in refluxing xylene, **1** afforded 1:2 adducts **9** and benzoxadiazole derivative **10** in 19 and 21% yields, respectively, accompanied by much intractable material. The ^1H NMR spectrum of **9** exhibited signals at δ 6.41, 6.81, 6.86, and 6.96 (each s, ca. 0.5 H), besides aromatic protons (20 H). Thus, it was deduced that **9** is a 1:1 mixture of 5-phenylisoxazole derivatives **9-2** and **9-4**. On the other hand, **1** reacted with methyl phenylpropiolate (**3e**) in refluxing xylene to give two isomeric 1:2 adducts **11** in 15 and 18% yields, respectively, together with tarry materials. In this case the corresponding benzoxadiazole derivative could not be isolated. Two isomeric 1:2 adducts were deduced to be 4-(methoxycarbonyl)-5-phenylisoxazole derivatives on the basis of spectral data,[8] although it was not clear which isomer would be **11-2** or **11-4**.

Reaction of 4,6-Diphenyl[3,4-*c*][1,2,5]thiadiazole (2). Contrary to the cycloadducts of **1** to *N*-phenylmaleimide, analogous cycloadducts formed from **2** undergo a retrocycloaddition reaction.[5] Thus, our attention was directed toward the reactions of **2** with acetylenes **3** in order to obtain information concerning the thermal behavior of the expected cycloadducts.

When an equimolar solution of **2** and the acetylene **3a** was refluxed for 1 h in xylene, the benzothiadiazole **12a** was obtained in good yield. Structural elucidation of **12a** was accomplished on the basis of spectral data and chemical conversion. Reductive desulfurization of **12a** with

Raney nickel afforded the *p*-terphenyl derivative **13** (see Scheme III).

Similarly, **2** reacted with acetylenes **3b–d** to give the corresponding desulfurized benzothiazoles **12b–d**, respectively, in good yields. Thus, it is evident that the initial strained cycloadducts undergo exclusively desulfurization under these reaction conditions.

The reaction conditions, yields, and physical and spectral data of **12** are summarized in Table I.

Experimental Section

Melting points were determined on a Yanagimoto micro-melting-point apparatus and were uncorrected. IR, NMR, and mass spectra were obtained on a JASCO IRA-1 spectrometer, Hitachi R-40 and JEOL SX-100 spectrometers, and a Hitachi RMS-4 spectrometer, respectively. IR and NMR spectra were taken in KBr disks and $CDCl_3$ solutions, respectively. Mass spectra were obtained at 70 eV.

Reaction of 4,6-Diphenylthieno[3,4-*c*][1,2,5]oxadiazole (1) with Dimethyl Acetylenedicarboxylate (3a). A solution of **1**[4] (870 mg, 3.1 mmol) and **3a** (440 mg, 3.1 mmol) in benzene (100 mL) was refluxed, under nitrogen, for 25.5 h. After the reaction mixture was cooled, filtration gave 141 mg (32%) of unreacted **1**. The filtrate was evaporated in vacuo, and the residue was chromatographed on silica gel. From the fractions with benzene–$CHCl_3$ (4:1) and $CHCl_3$ as eluants, benzoxadiazole **5a** and 1:2 adduct **4a** were isolated, respectively.

Recrystallization of **4a** from MeOH gave 233 mg (27%) of pure **4a**, mp 123–125 °C dec, as colorless prisms: IR 2230 (C≡N, very weak), 1740 cm^{-1} (C=O); ^1H NMR δ 3.38, 3.57, 3.59, 4.00 (each s, 3 H), 7.2–7.9 (m, 10 H); ^{13}C NMR δ 52.2, 52.9, 53.5 (OCH_3), 56.8, 67.3 (quaternary C), 113.9 (4-C of isoxazole ring), 116.9 (C≡N), 126.5, 127.7, 128.5, 128.9, 129.3, 129.5, 135.3, 136.6, 147.0 (Ar C), 156.4, 159.5, 161.3, 161.7, 162.2, 164.1 (3-C and 5-C of isoxazole ring, ester and imido C=O). Anal. Calcd for $C_{28}H_{22}N_2O_9S$: C, 59.79; H, 3.94; N, 4.98. Found: C, 59.68; H, 3.95; N, 4.98.

On the other hand, **5a** was also recrystallized from MeOH to give 25.7 mg (2%) of pure **5a**, mp 192.5–193.5 °C, as yellow prisms: IR 1735 cm^{-1} (C=O); ^1H NMR δ 3.62 (s, 6 H), 7.35–7.75 (m, 10 H). Anal. Calcd for $C_{22}H_{16}O_5N_2$: C, 68.03; H, 4.15; N, 7.21. Found: C, 67.74; H, 4.37; N, 7.05.

A similar reaction of **1** (500 mg, 1.8 mmol) with **3a** (510 mg, 3.6 mmol) in benzene (50 mL) afforded 543 mg (54%) of **4a** and 28.2 mg (4%) of **5a**, respectively, together with recovery of **3a** (107 mg, 21%).

Hydrolysis of 1:2 Adduct 4a. After a solution of **4a** (192 mg) in 97% H_2SO_4 (5 mL) was stirred on a water bath (43–46 °C) for 3 h, the reaction mixture was poured into ice–water. The resulting mixture was extracted with $CHCl_3$, and the extract was evaporated in vacuo to leave a residue which on trituration with MeOH gave crystals. Recrystallization from MeOH afforded 138 mg (70%) of the carbamoyl derivative **6**, mp 175–176 °C, as colorless prisms: IR 3600–3100 (NH), 1735, 1685 cm^{-1} (C=O); ^1H NMR δ 3.42, 3.53, 3.63, 4.03 (each s, 3 H), 5.8–6.3 (br, 2 H, NH, exchanged with D_2O), 7.1–7.9 (m, 10 H); ^{13}C NMR δ 52.4, 52.9, 53.5 (OCH_3), 65.2, 72.2 (quaternary C), 114.6 (4-C of isoxazole ring), 128.2, 128.5, 137.6, 138.1, 141.0, 144.0 (Ar C), 156.4, 159.8, 161.2, 162.2, 164.9, 171.1 (3- and 5-C of isoxazole ring, ester, imido, and amido C=O). Anal. Calcd for $C_{28}N_{24}N_2O_{10}S$: C, 57.93; H, 4.17; N, 4.83. Found: C, 57.92; H, 4.12; N, 4.74.

Reaction of 1 with Dibenzoylacetylene (3b). After a solution of **1** (500 mg, 1.8 mmol) and **3b** (842 mg, 3.6 mmol) in benzene (50 mL) was refluxed, under nitrogen, for 26.5 h, the solvent was evaporated in vacuo. The residue was chromatographed on silica gel with hexane–benzene (1:1) and benzene as eluants to give unreacted **3b** (183 mg, 22%), benzoxadiazole **5b**, and 1:2 adduct **4b**, respectively. Recrystallization of **4b** from AcOEt gave 890 mg (66%) of pure **4b**, mp 215–216 °C, as pale yellow prisms: IR 2230 (C≡N, very weak), 1660 cm^{-1} (C=O); ^1H NMR δ 7.0–8.1 (m). Anal. Calcd for $C_{48}H_{30}N_2O_5S$: C, 77.20; H, 4.05; N, 3.75. Found: C, 77.18; H, 4.03; N, 3.54.

Recrystallization of **5b** from EtOH–$CHCl_3$ gave 39 mg (5%) of pure **5b**, mp 247.5–248.5 °C, as yellow prisms: IR 1660 cm^{-1} (C=O); ^1H NMR δ 7.1–7.9 (m). Anal. Calcd for $C_{32}H_{20}N_2O_3$: C, 79.98; H, 4.20; N, 5.83. Found: C, 80.00; H, 4.19; N, 5.66.

Table I. Reaction of Thienothiadiazole 2 with Acetylenes 3

acetylene	reaction conditions[a] solvent	time, h	product[b]	yield, %	mp, °C	^1H NMR ($CDCl_3$), δ	formula	anal. found (calcd) C	H	N	M^+, *m/e*
3a	xylene	1	**12a**	75	192–192.5	3.62 (s, 6 H), 7.45–7.7 (m, 10 H)	$C_{22}H_{16}N_2O_4S$	65.25 (65.34)	3.90 (3.99)	7.04 (6.93)	404
3b	xylene	1	**12b**	78	204.5–205.5	6.9–8.0 (m)	$C_{32}H_{20}N_2O_2S$	77.41 (77.40)	4.08 (4.06)	5.69 (5.64)	496
3c	toluene	48	**12c**	89	177–177.5	3.70 (s, 3 H), 7.45–7.8 (m, 8 H), 7.95–8.1 (m, 2 H), 8.16 (s, 1 H)	$C_{20}H_{14}N_2O_2S$	69.19 (69.36)	4.11 (4.07)	8.07 (8.09)	346
3d	xylene	48	**12d**	79	189.5–190.5	7.05–8.15 (m)	$C_{24}H_{16}N_2S$	78.91 (79.10)	4.47 (4.43)	7.65 (7.69)	364
3e	xylene	168	**12e**	84	172.5–173.5	3.26 (s, 3 H), 7.1–7.7 (m, 15 H)	$C_{26}H_{18}N_2O_2S$	73.71 (73.92)	4.36 (4.30)	6.68 (6.63)	422

[a] Refluxed in the cited solvent. [b] **12a**: yellow green prisms (from AcOEt), ν_{CO} 1715 cm^{-1}. **12b**: yellow prisms (from AcOEt), ν_{CO} 1655 cm^{-1}. **12c**: yellow green prisms (from MeOH), ν_{CO} 1730 cm^{-1}. **12d**: yellow needles (from EtOH). **12e**: yellow prisms (from MeOH), ν_{CO} 1730 cm^{-1}.

Reaction of 1 with Methyl Propiolate (3c). After a solution of **1** (1.0 g, 3.6 mmol) and **3c** (605 mg, 7.2 mmol) in benzene (100 mL) was refluxed, under nitrogen, for 36 h, the solvent was evaporated in vacuo. The residue was chromatographed on silica gel with benzene–hexane (1:1) and benzene–$CHCl_3$ (1:1) as eluants to give 365 mg (31%) of benzoxadiazole **8** and 571 mg (36%) of a mixture of **7**, respectively.

Mixture of **7**: mp 62–67 °C; yellow crystals; IR 2240 (C≡N, very weak), 1730 cm^{-1} (C=O); ^1H NMR δ 3.51, 3.61, 3.64, 3.84 (each s), 7.05–7.8 (m), 9.0, 9.05 (each s) (the relative intensities of signals of OCH_3, aromatic region, and 5-H of isoxazole ring were 58:127:1). Anal. Calcd for $C_{24}H_{18}N_2O_5S$: C, 64.57; H, 4.06; N, 6.28. Found: C, 64.59; H, 4.08; N, 6.15. Attempts to isolate pure 1:2 adduct(s) **7** by chromatography or fractional recrystallization were unsuccessful.

Recrystallization of **8** from MeOH afforded pure **8**, mp 104–105 °C, as yellow prisms: IR 1715 cm^{-1} (C=O); ^1H NMR δ 3.67 (s, 3 H), 7.1–8.1 (m, 11 H). Anal. Calcd for $C_{20}H_{14}N_2O_3$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.69; H, 4.18; N, 8.44.

Reaction of 1 with Phenylacetylene (3d). After a solution of **1** (1.0 g, 3.6 mmol) and **3d** (734 mg, 7.2 mmol) in xylene (100 mL) was refluxed, under nitrogen, for 2.5 h, the solvent was evaporated in vacuo to leave a residue which was chromatographed on silica gel. From the fractions with hexane–benzene (3:1 and 1:3) as eluants, 269 mg (21%) of benzoxadiazole **10** and 324 mg (19%) of a mixture of 1:2 adducts **9** were obtained, respectively. Further elution using benzene and $CHCl_3$ gave intractable materials.

Mixture of **9**: mp 83–90 °C; pale red crystals; IR 2230 cm^{-1} (C≡N, very weak); ^1H NMR δ 6.41, 6.81, 6.86, 6.96 (each s, ca. 0.5 H), 6.9–8.0 (m, 20 H). Anal. Calcd for $C_{32}H_{22}N_2OS$: C, 79.65; H, 4.60; N, 5.81. Found: C, 79.64; H, 4.84; N, 5.85. Attempts to isolate pure **9** were unsuccessful.

Recrystallization of **10** from MeOH gave pure **10**, mp 188–189 °C, as yellow prisms: ^1H NMR δ 6.8–7.6 (m, 13 H), 7.69 (s, 1 H), 7.9–8.1 (m, 2 H). Anal. Calcd for $C_{24}H_{16}N_2O$: C, 82.74; H, 4.63; N, 8.04. Found: C, 82.74; H, 4.63; N, 7.94.

Reaction of 1 with Methyl Phenylpropiolate (3e). A solution of **1** (1.0 g, 3.6 mmol) and **3e** (1.15 g, 7.2 mmol) in xylene (100 mL) was refluxed, under nitrogen, for 9 h. The solvent was evaporated in vacuo, and the residue was triturated with MeOH (10 mL) to give colorless crystals which on recrystallization from AcOEt gave 323 mg (15%) of 1:2 adduct **11-2** (or **11-4**), mp 250–251 °C, as colorless prisms: IR 2230 (C≡N, very weak), 1720 cm^{-1} (C=O); ^1H NMR δ 3.17, 3.30 (each s, 3 H), 6.8–8.1 (m, 20 H). Anal. Calcd for $C_{36}H_{26}N_2O_5S$: C, 72.23; H, 4.38; N, 4.68. Found: C, 71.94; H, 4.31; N, 4.61.

The MeOH mother liquor was concentrated in vacuo to leave a residue which on chromatography on silica gel using benzene and $CHCl_3$ as eluants gave pale yellow crystals and intractable materials, respectively. Recrystallization of the crystals from EtOH afforded 404 mg (18%) of 1:2 adduct **11-4** (or **11-2**), mp 178–180 °C dec, as pale yellow prisms: IR (2240 (C≡N, very weak), 1730 cm^{-1} (C=O); ^1H NMR 3.23, 3.30 (each s, 3 H), 7.0–8.15 (m, 20 H). Anal. Calcd for $C_{36}H_{26}N_2O_5S$: C, 72.23; H, 4.38; N, 4.68. Found: C, 71.96; H, 4.38; N, 4.60.

Reaction of 4,6-Diphenylthieno[3,4-*c*][1,2,5]thiadiazole (2) with Acetylene 3a. A solution of **2**[9] (200 mg, 0.68 mmol) and **3a** (97 mg, 0.68 mmol) in xylene (10 mL) was refluxed, under nitrogen, for 1 h. The solvent was evaporated in vacuo, and the residue was chromatographed on silica gel with benzene as eluant to give crystals. Recrystallization from AcOEt gave 200 mg (73%) of benzothiadiazole **12a**.

Similarly, **2** reacted with acetylenes **3b–3e** to afford the corresponding benzothiadiazoles **12b–12e**. The reaction conditions, yields, and physical and analytical data of **12** are summarized in Table I.

Reductive Desulfurization of Benzothiadiazole 12a. A solution of **12a** (67 mg) in MeOH (10 mL) was stirred with W-2 Raney nickel catalyst (ca. 0.6 g) under reflux for 2 h. After the reaction mixture was filtered, the filtrate was concentrated to about one-half its initial volume. Filtration of precipitates and recrystallization from MeOH afforded 30 mg (48%) of *p*-terphenyl derivative **13**, mp 204.5–205.5 °C, as colorless prisms: IR 3440, 3350 (NH), 1705, 1690 cm^{-1} (C=O); ^1H NMR δ 2.9–3.3 (br, 4 H, NH_2, exchanged with D_2O), 3.44 (s, 6 H), 7.25–7.65 (m, 10 H); mass spectrum, *m/e* 376 (M^+, base peak). Anal. Calcd for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44. Found: C, 69.85; H, 5.47; N, 7.47.

Registry No. 1, 64959-93-9; 2, 24793-62-2; **3a**, 762-42-5; **3b**, 1087-09-8; **3c**, 922-67-8; **3d**, 536-74-3; **3e**, 4891-38-7; **4a**, 73770-70-4; **4b**, 73770-71-5; **5a**, 73770-72-6; **5b**, 73770-73-7; **6**, 73770-74-8; **7-1**, 73770-75-9; **7-2**, 73770-76-0; **7-3**, 73770-77-1; **7-4**, 73770-78-2; **8**, 73770-79-3; **9-2**, 73770-80-6; **9-4**, 73770-81-7; **10**, 73770-82-8; **11-2**, 73770-83-9; **11-4**, 73770-84-0; **12a**, 73770-85-1; **12b**, 73770-86-2; **12c**, 73770-87-3; **12d**, 73770-88-4; **12e**, 73770-89-5; **13**, 73770-90-8.

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Facile Syntheses of 1,3-Dithiol-2-ones and 1,3-Dithiole-2-thiones

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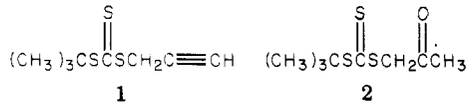
A facile ring closure of allyl xanthates or trithiocarbonates with iodine is discussed. The products of the reaction undergo basic dehydroiodination and acidic isomerization to give 1,3-dithiol-2-ones and -2-thiones in high yield.

Recently we reported a novel synthesis of 1,3-dithiole-2-thiones from sodium *tert*-butyl trithiocarbonate and propargyl halides via the acid-catalyzed ring closure of the intermediate propargyl *tert*-butyl trithiocarbonate (**1**).[1]



1 **2**

Later we expanded the scope of this synthesis to include the cyclization of β-oxo *tert*-butyl trithiocarbonates (**2**) to 1,3-dithiole-2-thiones.[2] We now report a still more general synthetic route to the 1,3-dithiole system which includes an efficient synthesis of 1,3-dithiol-2-ones.[3] The synthetic path is illustrated in Scheme I. At first glance, the new

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