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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(10) M. Christl, R. Huisgen, and R. Sustmann, *Chem. Ber.*, **106**, 3275 (1973).
(11) K. Bast, M. Christl, R. Huisgen, W. Mack, and R. Sustmann, *Chem. Ber.*, **106**, 3258 (1973).

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

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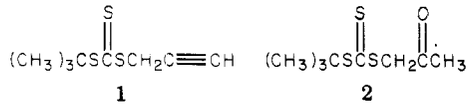
A facile ring closure of allyl xanthates or trithiocarbonates with iodine is discussed. The products of the reaction undergo basic dehydroiodination and acidic isomerization to give 1,3-dithiol-2-ones and -2-thiones in high yield.

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**

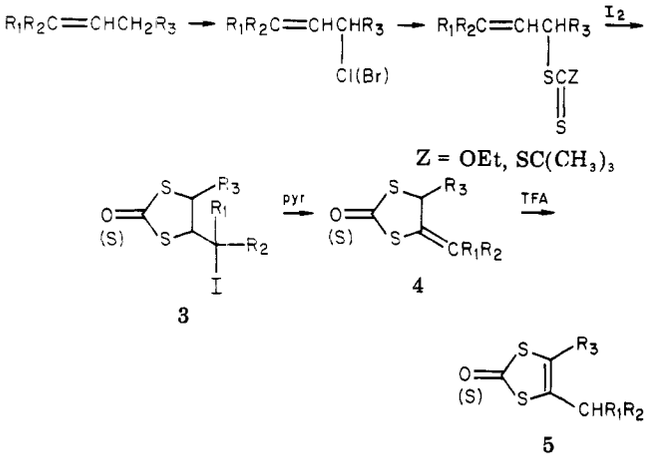
Later we expanded the scope of this synthesis to include the cyclization of β-oxo *tert*-butyl trithiocarbonates (**2**) to 1,3-dithiole-2-thiones.[2] We now report a still more general synthetic route to the 1,3-dithiole system which includes an efficient synthesis of 1,3-dithiol-2-ones.[3] The synthetic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

(1) Haley, N. F. *Tetrahedron Lett.* **1978**, 5161.

(2) Haley, N. F.; Fichtner, M. *J. Org. Chem.* **1980**, *45*, 175.
(3) We have also produced 1,3-dithiol-2-ones by the acid-catalyzed ring closure of ethyl xanthate esters derived from propargyl halides and KSCSOEt (**1**) (unpublished results). For other syntheses, see: (a) Bhattacharya, A. K.; Hortmann, A. G. *J. Org. Chem.* **1974**, *39*, 95 and references cited therein; (b) Benitez, F. M.; Grunwall, J. R. *J. Org. Chem.* **1978**, *43*, 2917.

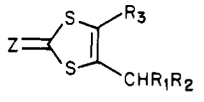
0022-3263/80/1945-2959$01.00/0

Scheme I



3 4 5

Table I. Yields of 1,3-Dithiol-2-ones and -thiones (5)



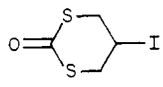
5

	R_1	R_2	R_3	Z	yield of 5, %[a]
a	H	H	H	O	97
b	CH_3	H	H	O	83
c	CH_3	CH_3	H	O	94
d	n-C_5H_{11}	H	H	O	77
e	C_5H_5	H	H	O	86
f	C_6H_5	H	H	S	80
g	H	$CH_2CH_2CH_2$		O	63
h	H	H	H	S	50
i	CH_3	CH_3	H	S	57

[a] Based on purified material starting from the allyl halide (Scheme I).

route may appear laborious (5 steps), but the rapid and efficient nature of each step makes the overall synthesis surprisingly simple. It also allows one to begin with simple olefins which are more readily available than the substituted α-halo ketones or propargyl halides which were necessary in earlier syntheses.[4] The yields shown in Table I for the 1,3-dithioles are based on the corresponding starting allyl halide. The intermediates are produced nearly quantitatively and pure enough to use in the next synthetic step, leaving at the end only a simple distillation or recrystallization of the final 1,3-dithiole. The entire reaction sequence takes 4–6 h.[5]

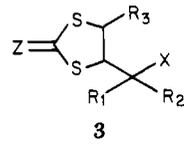
The key transformation in the syntheses is the formation of the 1,3-dithiolane ring (3) (Table II) from the corresponding allyl xanthate or trithiocarbonate ester and iodine, with a concomitant loss of either ethyl iodide or isobutylene/HI, as illustrated in Scheme II.[6] The halocyclization of allyl xanthates or trithiocarbonate esters produces just 1,3-dithiolanes (3), with no detectable amount of the corresponding 1,3-dithiane (6).



6

(4) For instance, **5d** would require either $ClCH_2COC_6H_{13}$ or $ClCH_2C{\equiv}CC_5H_{11}$ by our other syntheses.[1,2] 1-Octene is more readily available.
(5) Starting from the allyl halide.
(6) Bromine performs equally well; however, the next step, dehydrohalogenation, occurs more readily with iodine.

Table II. 1,3-Dithiolanes via Halogenation

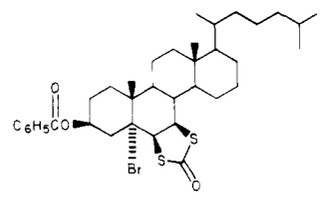


3

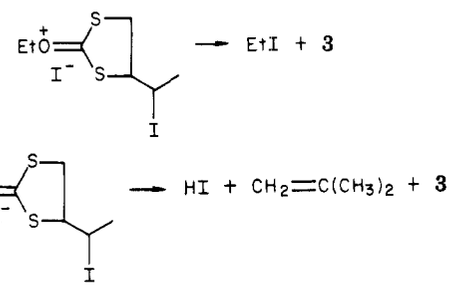
	R_1	R_2	R_3	Z	X	yield of 3, %[a]
a	H	H	H	O	Br	98
b	H	H	H	O	I	97
c	CH_3	H	H	O	I	
d	CH_3	CH_3	H	O	I	98
e	n-C_5H_{11}	H	H	O	I	
f	C_6H_5	H	H	O	I	
g	C_6H_5	H	H	S	I	91
h	H	$CH_2CH_2CH_2$		O	I	
i		[b]				86
j	H	H	H	S	I	
k	CH_3	CH_3	H	S	I	

[a] In reactions where intermediate 3 was isolated.

[b]



Scheme II



The structure of 3 was confirmed by ^{13}C and ^1H NMR. Similar to our studies, those of Nakai et al. showed that bromination of *N*-allyldithiocarbamate derivatives also leads only to five-membered-ring products.[7] McManus and co-workers, having studied this phenomenon of five- vs. six-membered-ring closure, postulate an anchimerically assisted route rather than carbocation formation to explain the fact that only five-membered rings are formed in Nakai's experiments.[8] We propose a similar mechanism for our ring closure of allyl xanthates and trithiocarbonates; however, our intermediate ions (see Scheme II) are unstable and lose ethyl iodide or isobutylene, forming 3 as the stable product.[9]

We also observed that only anti addition product 3 is formed, which is consistent with a halonium ion intermediate. Mixtures of diastereomers of 3 are found only when the starting olefinic xanthate ester is a cis/trans mixture or long iodination times are used (24 instead of 2 h).[10] These mixtures of diastereomers, however, present no problem, since the elimination and isomerization elim-

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(8) McManus, S. P.; Ware, D. W.; Hames, R. A. *J. Org. Chem.* **1978**, *43*, 4288.
(9) Nakai's initial 2-(dialkylammonio)-1,3-dithiolanium ion was stable and precipitated from solution as a bromide salt. In the closure of trithiocarbonates, but not xanthates, we observed an intermediate precipitate which quickly redissolved.
(10) Ring closure to **5f** was stereospecific if iodination was allowed to proceed for only 1 h; after 24 h a 3:1 mixture of diastereomers was present.

inate any stereospecificity in the final product (**5**). However, as an example of the stereospecificity and selectivity of the halogenation, 7α-bromocholesterol benzoate formed the brominated 1,3-dithiolane (**3i**) in 86% yield with only the stereochemistry shown in Table II (by NMR).[12,15]

Dehydroiodination of **3** in pyridine is exothermic and complete in minutes at 100 °C, yielding **4**. In contrast, dehydrobromination of **3a** is only 5% complete after extensive reflux in pyridine (3 h). Thus iodine is the reagent of choice for ring closure under these conditions. The reaction sequence is completed by isomerization of **4** to dithiole **5** in refluxing trifluoroacetic acid. Thus, we have found the synthetic sequence (Scheme I) to be useful for the preparation of many 1,3-dithiol-2-ones and -2-thiones (Table I) and in some cases the method of choice (e.g., **5d**).

Experimental Section

All boiling points and melting points are uncorrected. IR spectra were obtained on a Perkin-Elmer Model 137 infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM390 spectrometer with Me_4Si as an internal standard. ^{13}C NMR spectra were recorded on a Brüker spectrometer with Me_4Si as an internal standard. Mass spectra were taken on an AEI MS90 mass spectrometer with an ionizing potential of 70 eV. Microanalyses were done by Carol Brown of our microanalytical laboratory. All allyl bromides were obtained from commercial sources except 1-bromo-2-octene[11] and 7-bromocholesterol benzoate.[12]

General Procedure for the Synthesis of 5. An allyl halide (0.1 mol) and potassium ethyl xanthate or sodium *tert*-butyl trithiocarbonate[2] (0.1 mol) were stirred at 0–10 °C in 200 mL of acetone for about 1 h. The insoluble inorganic halide was separated, and the acetone solution was evaporated under vacuum. The residue was dissolved in 250 mL of methylene chloride at 0 °C and treated with 0.1 mol of iodine or bromine. The resulting solution was stirred at room temperature for 1 h. Saturated sodium bicarbonate solution (50 mL) was added, followed by portions of solid sodium bisulfite until the organic layer was pale yellow. The organic phase was separated, dried ($MgSO_4$), and evaporated under vacuum. The residue (**3**) was dissolved in 200 mL of pyridine and heated on a steam bath for 1 h; 200 mL of water was added and the mixture was extracted twice with 200-mL portions of cyclohexane or ether. After the organic phase was dried and evaporated, the residue (**4**) was dissolved in a minimum amount of trifluoroacetic acid and refluxed for 1 h. The reaction mixture was cooled and 100 mL of water was added, followed by extraction with 100 mL of cyclohexane or ether. The organic phase was washed with $NaHCO_3$ solution, dried ($MgSO_4$), and evaporated under vacuum. The residue was either distilled or recrystallized to give the pure 1,3-dithiole (**5**). Each intermediate could be isolated and purified, but this did not significantly increase the yields of **5**.[13]

***S*-Allyl *O*-Ethyl Dithiocarbonate.** This compound was obtained in 100% yield from potassium ethyl xanthate and 3-bromo-1-propene and used directly: ^{1}H NMR ($CDCl_3$) δ 6.2–5.0 (m, 3 H), 4.6 (q, 2 H), 3.7 (d, 2 H), 1.4 (t, 3 H).

***S*-Buten-2-yl *O*-Ethyl Dithiocarbonate.** This compound was obtained in 96% yield from 1-bromo-2-butene: ^{1}H NMR ($CDCl_3$) δ 5.9–5.3 (m, 2 H), 4.6 (q, 2 H), 3.7 (m, 2 H), 1.4 (t, 3 H).

Anal. Calcd for $C_7H_{12}OS_2$: C,47.7; H, 6.9; S, 36.4. Found: C, 47.5; H, 7.2; S, 36.6.

***S*-Cinnamyl *O*-Ethyl Dithiocarbonate.** This compound was obtained in 97% yield from cinnamyl bromide and used directly: ^{1}H NMR ($CDCl_3$) δ 7.4 (m, 5 H), 6.7 (d, J = 15 Hz, 1 H), 6.3 (d of t, J = 15 Hz, J = 7 Hz, 1 H), 4.7 (q, 2 H), 4.0 (d, J = 7 Hz, 2 H), 1.5 (t, 3 H).

***S*-Cyclohexen-3-yl *O*-Ethyl Dithiocarbonate.** This compound was obtained in 97% yield from 3-bromocyclohexene and used directly: ^{1}H NMR ($CDCl_3$) δ 5.7 (m, 2 H), 4.6 (q, 2 H), 4.3 (m, 1 H), 2.0 (m, 4 H), 1.7 (m, 2 H), 1.4 (t, 3 H).

***S*-(3-Methyl-2-buten-1-yl) *O*-Ethyl Dithiocarbonate.** This compound was obtained in 100% yield from 1-bromo-3-methyl-2-butene: ^{1}H NMR ($CDCl_3$) δ 5.3 (t of q, 1 H), 4.6 (q, 2 H), 3.7 (d, 2 H), 1.7 (d of d, 6 H), 1.4 (t, 3 H).

Anal. Calcd for $C_8H_{14}OS_2$: C, 50.5; H, 7.4; S, 33.7. Found: C, 50.7; H, 7.6; S, 33.6.

***S*-(2-Octen-1-yl) *O*-Ethyl Dithiocarbonate.** This compound was obtained in 87% yield from a mixture of 1-bromo-2-octene and 3-bromo-1-octene and used directly: ^{1}H NMR ($CDCl_3$) δ 5.8–5.2 (m, 2 H), 4.6 (q, 2 H), 3.7 (d, 2 H), 2.0 (m, 2 H), 1.4 (m, 9 H), 0.9 (m, 3 H).

***S*-(3β-(Benzyloxy)-5-cholesten-7β-yl) *O*-Ethyl Dithiocarbonate.** This compound was obtained in 100% yield from 7α-bromocholesterol benzoate: mp 83–84 °C (CH_2Cl_2–CH_3OH); ^{1}H NMR ($CDCl_3$) δ 8.1 (m, 2 H), 7.5 (m, 3 H), 5.5 (d, J = 2 Hz, 1 H), 4.8 (m, 1 H), 4.6 (q, 2 H), 4.1 (d, J = 8 Hz, 1 H), 2.5 (br d, 2 H), 2.1–0.5 (m, 42 H).

Anal. Calcd for $C_{37}H_{54}O_3S_2$: C, 72.7; H, 8.9; S, 10.5. Found: C, 72.6; H, 8.6; S, 10.2.

Cinnamyl *tert*-Butyl Trithiocarbonate. This compound was obtained in 100% yield from cinnamyl bromide and sodium *tert*-butyl trithiocarbonate:[2] ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.6 (d of t, J = 16, J = 0.6 Hz, 1 H), 6.2 (d of t, J = 16, J = 7 Hz, 1 H), 4.1 (d of d, J = 7, J = 0.6 Hz, 2 H), 1.6 (s, 9 H).

Anal. Calcd for $C_{14}H_{18}S_3$: C, 59.5; H, 6.4; S, 34.1. Found: C, 59.5; H, 6.3; S, 34.1.

4-(Iodomethyl)-1,3-dithiolan-2-one (3b): IR (neat) 1724 (w), 1639 (s), 1408, 1176, 877, 847 cm^{-1}; mass spectrum, m/e 260, 232, 167, 159, 133, 127, 105, 91, 73, 59, 47, 45, 39; ^{13}C NMR ($CDCl_3$) δ 194.8 (C=O), 52.0 (CHS), 40.0 (CH_2S), 5.5 (CH_2I) (decoupled spectrum); ^{1}H NMR ($CDCl_3$) δ 4.1 (sextet with finer splitting, 1 H), 3.8–3.3 (m, 4 H).

Anal. Calcd for $C_4H_5IOS_2$: C, 18.5; H, 2.0; S, 24.7. Found: C, 18.5; H, 2.0; S, 25.0.

4-(Bromomethyl)-1,3-dithiolan-2-one (3a): IR (neat) 1695, 1639, 1418, 1235, 1198, 939, 893, 847 cm^{-1}; mass spectrum, m/e 212 (M^+), 184, 152, 121, 119, 73, 59, 43.

Anal. Calcd for $C_4H_5BrOS_2$: C, 22.5; H, 2.4; Br, 37.5; S, 30.1. Found: C, 22.6; H, 2.5; Br, 37.6; S, 29.9.

Refluxing for 3 h in pyridine gave only 5% elimination product (**4a**) as determined by NMR.

4-(2-(2-Iodopropyl))-1,3-dithiolan-2-one (3d): IR (neat) 1739, 1652, 1087, 869 cm^{-1}; NMR ($CDCl_3$) δ 4.3 (d of d, 1 H), 3.8 (m, 2 H), 2.1 (s, 3 H).

Anal. Calcd for $C_6H_9IOS_2$: C, 25.0; H, 3.1; S, 22.3. Found: C, 24.7; H, 3.0; S, 21.9.

4-(α-Iodobenzyl)-1,3-dithiolan-2-one (3g): mp 118–119 °C (EtOH); IR (KBr) 1626, 1110, 893, 760, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 5.3 (d, J = 11 Hz, 1 H), 4.7 (m, 1 H), 4.0 (d of d, J = 12 Hz, J = 6 Hz, 1 H), 3.7 (d of d, J = 12 Hz, J = 7.6 Hz, 1 H); mass spectrum, m/e 337 (M + 1), 254, 209, 181, 149, 117, 91, 77, 60, 45.

Anal. Calcd for $C_{10}H_9IOS_2$: C, 35.7; H, 2.7; S, 19.1. Found: C, 36.0; H, 2.5; S, 18.7.

3β-(Benzyloxy)-5α-bromocholestano[6β,7β-*d*]-1′,3′-dithiolan-2′-one (3i): mp 156–157 °C (CH_2Cl_2 + MeOH); IR (KBr) 2899, 1709, 1650, 1266, 1109, 877, 714 cm^{-1}; mass spectrum, m/e 580, 458, 398, 365, 190, 157, 122, 105; ^{1}H NMR ($CDCl_3$) δ 5.6 (m, 1 H, H_3), 5.1 (d, J = 5 Hz, 1 H, H_6), 4.5 (d of d, J = 5 Hz, J = 10 Hz, 1 H, H_7).[15]

Anal. Calcd for $C_{35}H_{49}BrO_3S_2$: C, 63.5; H, 7.5; S, 9.7. Found: C, 63.6; H, 7.1; S, 9.4.

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(13) Distillation of the intermediate thioesters and iodo-1,3-dithiolanes gave extensive decomposition; consequently, boiling points are reported only for those compounds that were successfully distilled.

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(15) The stereochemical assignments of **3i** were based on the NMR coupling constants between H_6, H_7, and H_8 and comparisons with model compounds cited in ref 12. The chemical shifts of H_6 and H_7 were determined by using double-resonance techniques. Johnson and Lack[12] showed that the 7α-proton in 7β-acetoxycholesterol benzoate is coupled to H_8 with J = 9 Hz (trans), and in 7α-acetoxycholesterol benzoate the 7β-proton is coupled to H_8 with J = 0–2 Hz (cis). We observed a J value of 8 Hz in *S*-7-(benzoyloxy)cholesteryl *O*-ethyl dithiocarbonate, indicating the β configuration for the xanthate group. Ring closure is expected to generate a cis-fused dithiole ring, consequently placing the bromine in the 5α position as in **3i**. This is suggested by J_{7-8} = 10 Hz and J_{6-7} = 5 Hz.

4-Methyl-1,3-dithiol-2-one (5a). This compound was obtained pure by evaporative distillation (kugelrohr) at 90 °C (12 mmHg): ^{1}H NMR ($CDCl_3$) δ 6.3 (q, J = 1.4 Hz, 1 H), 2.3 (d, J = 1.4 Hz, 3 H); IR (neat) 1740, 1670, 1640 cm^{-1}; UV (EtOH) 269 (3.38), 238 (3.39), 212 (3.37) nm (log ϵ).

Anal. Calcd for $C_4H_4OS_2$: C, 36.4; H, 3.0; S, 48.5. Found: C, 36.5; H, 3.1; S, 48.4.

4-Ethyl-1,3-dithiol-2-one (5b). This compound was obtained pure by evaporative distillation (kugelrohr) at 60 °C (0.10 mmHg): ^{1}H NMR ($CDCl_3$) δ 6.2 (t, J = 1.8 Hz, 1 H), 2.6 (q of d, J = 9, J = 1.8 Hz, 2 H), 1.2 (t, J = 9 Hz, 3 H); IR (neat) 1739, 1653, 1563, 870 cm^{-1}.

Anal. Calcd for $C_5H_6OS_2$: C, 41.1; H, 4.1; S, 43.9. Found: C, 41.3; H, 4.1; S, 43.6.

4-Isopropyl-1,3-dithiol-2-one (5c). This compound was obtained pure by evaporative distillation at 70 °C (0.10 mmHg): ^{1}H NMR ($CHCl_3$) δ 6.4 (d, J = 1.5 Hz, 1 H), 2.9 (septet of doublets, J = 1.5, J = 6.7 Hz, 1 H), 1.3 (d, J = 6.7 Hz, 6 H); IR (neat) 1754, 1653, 1574, 869 cm^{-1}; mass spectrum, m/e 160 (M^+), 145, 132, 117, 99, 87, 53, 45, 41, 39.

Anal. Calcd for $C_6H_8OS_2$: C, 45.0; H, 5.0; S, 40.0. Found: C, 45.1; H, 4.9; S, 39.7.

4-*n*-Hexyl-1,3-dithiol-2-one (5d). This compound was obtained pure by evaporative distillation (kugelrohr) at 85 °C (0.15 mmHg): ^{1}H NMR ($CDCl_3$) δ 6.3 (t, J = 1.2 Hz, 1 H), 2.6 (t of d, J = 1.2, J = 6.6 Hz, 2 H), 1.4–0.9 (m, 11 H).

Anal. Calcd for $C_9H_{14}OS_2$: C, 53.5; H, 6.9; S, 31.7. Found: C, 53.4; H, 6.9; S, 32.0.

4-Benzyl-1,3-dithiol-2-one (5e). This compound was obtained pure by evaporative distillation (kugelrohr) at 195 °C (20 mmHg); mp (EtOH) 38–40 °C; ^{1}H NMR ($CDCl_3$) δ 7.2 (m, 5 H), 6.3 (t, J = 1.2 Hz, 1 H), 3.8 (d, J = 1.2 Hz, 2 H); UV (EtOH) 265 (3.52), 242 (3.60) nm (log ϵ); IR (neat) 1724, 1645, 1563, 1493, 1449, 862, 760, 690 cm^{-1}; mass spectrum, m/e 208, 180, 179, 147, 135, 117, 115, 91.

Anal. Calcd for $C_{10}H_8OS_2$: C, 57.7; H, 3.8; S, 30.8. Found: C, 58.0; H, 3.8; S, 30.9.

4-Benzyl-1,3-dithiole-2-thione (5d). This compound was obtained by evaporative distillation at 195 °C (0.1 mmHg): ^{1}H NMR ($CDCl_3$) δ 7.1 (m, 5 H), 6.4 (t, J = 1 Hz, 1 H), 3.8 (d, J = 1 Hz, 2 H). In contrast, 4-benzylidene-1,3-dithiolane-2-thione had ^{1}H NMR ($CDCl_3$) δ 7.3 (m, 5 H), 6.7 (t, J = 2 Hz, 1 H), 4.7 (d, J = 2 Hz, 2 H).

Anal. Calcd for $C_{10}H_8S_3$: C, 53.6; H, 3.5; S, 42.9. Found: C, 53.2; H, 3.4; S, 43.1.

Cyclohexano[*d*]-1,3-dithiol-2-one (5g). This compound was obtained by evaporative distillation at 90 °C (0.05 mmHg). NMR and IR spectra were identical with those of a known sample.[3a]

4-Methyl-1,3-dithiole-2-thione (5h). This compound was obtained by distillation: bp 90–93 °C (0.05 mmHg); mp 28–30 °C (lit.[14] 30 °C); ^{1}H NMR ($CDCl_3$) δ 6.7 (q, J = 1.2 Hz, 1 H), 2.3 (d, J = 1.2 Hz, 3 H).

4-Isopropyl-1,3-dithiole-2-thione (5i). This compound was obtained by distillation: bp 89–91 °C (0.05 mmHg); ^{1}H NMR ($CDCl_3$) δ 6.7 (d, J = 1.2 Hz, 1 H), 3.0 (septet of d, J = 1.2, J = 7.0 Hz, 1 H), 1.3 (d, J = 7.0 Hz, 6 H).

Anal. Calcd for $C_6H_8S_3$: C, 40.9; H, 4.5; S, 54.6. Found: C, 41.2; H, 4.9; S, 54.2.

Registry No. 3a, 73872-16-9; **3b**, 73872-17-0; **3d**, 73872-18-1; **3g**, 73872-19-2; **3i**, 73872-20-5; **5a**, 42574-01-6; **5b**, 73872-21-6; **5c**, 73872-22-7; **5d**, 73872-23-8; **5e**, 73872-24-9; **5f**, 6136-08-9; **5g**, 698-41-9; **5h**, 3608-38-6; **5i**, 73872-25-0; *S*-allyl *O*-ethyl dithiocarbonate, 7124-50-7; potassium ethyl xanthate, 140-89-6; 3-bromo-1-propene, 106-95-6; *S*-buten-2-yl *O*-ethyl dithiocarbonate, 73872-26-1; 1-bromo-2-butene, 4784-77-4; *S*-cinnamyl *O*-ethyl dithiocarbonate, 73872-27-2; cinnamyl bromide, 4392-24-9; *S*-cyclohexen-3-yl *O*-ethyl dithiocarbonate, 73872-28-3; 3-bromocyclohexene, 3540-84-9; *S*-(3-methyl-2-buten-1-yl) *O*-ethyl dithiocarbonate, 73872-29-4; 1-bromo-3-methyl-2-butene, 870-63-3; *S*-(2-octen-1-yl) *O*-ethyl dithiocarbonate, 73872-30-7; 1-bromo-2-octene, 25466-54-0; 3-bromo-1-octene, 40906-92-1; *S*-(3β-(benzoyloxy)-5-cholesten-7β-yl) *O*-ethyl dithiocarbonate, 73872-31-8; 7α-bromocholesterol, 26048-46-4; cinnamyl *tert*-butyl trithiocarbonate, 73872-32-9; sodium *tert*-butyl trithiocarbonate, 71127-42-9.

Organic Fluorine Compounds. 32.[1] A 1,3-Dipolar Cycloaddition Reaction of Tetrakis(trifluoromethyl)(Dewar Thiophene) and Some Reactions of the Cycloadducts[2]

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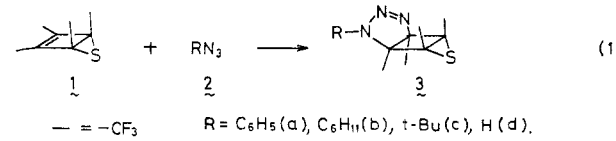
The reaction of tetrakis(trifluoromethyl)(Dewar thiophene) (**1**) with azide compounds **2**, including hydrogen azide, gave high yields of 1,3-dipolar cycloadducts **3**. Compounds **3a–d** were desulfurized with triphenylphosphine to afford cyclobutatriazoline compounds **4a–d**, which were converted thermally to the diazo imine compounds **5a–d** by a retro-1,3-dipolar reaction. Compounds **5a–d** were denitrogenated to pyrrole compounds **7a,b,d** and/or cyclopropenylimines **8b,c** on thermolysis. The adducts **2a–d** were ring opened thermally to diazothiirane compounds **9a–d**, which were further converted to thiete compounds **10a–d**.

Tetrakis(trifluoromethyl)(Dewar thiophene) (**1**) has a strained double bond substituted with highly electronegative trifluoromethyl groups and is known to be a good dienophile in Diels–Alder reactions.[3] We have now found that **1** undergoes 1,3-dipolar cycloaddition with azides. The 4,5-dihydro-1,2,3-triazoles formed in this way were thermally cleaved to diazo imines.

Results and Discussion

Treatment of **1** with azides **2a–d** at room temperature gave the corresponding 1,3-dipolar cycloadducts **3a–d** in good yield[2a,b] (eq 1). The isolated cycloadducts are stable



(1)

1 — = —CF_3 **2** R = C_6H_5(a), C_6H_{11}(b), t-Bu(c), H(d). **3**

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