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A Convenient Synthesis of 1,2-Dithietes and 1,2-Dithioxo Compounds Stabilized by Buttressing and Resonance Effects, Respectively, by Sulfuration of Alkynes with Elemental Sulfur

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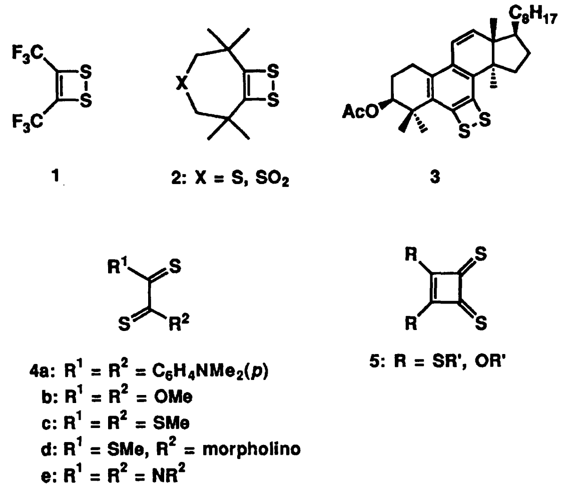
Sulfuration of a series of alkynes by elemental sulfur was investigated. Alkynes carrying highly bulky substituents, 2,2,5,5-tetramethyl-3-hexyne (**6a**), 1,2-di-(1-adamantyl)ethyne (**6b**), 3,3-dimethyl-1-phenyl-1-butyne (**6c**), and 1-(1-adamantyl)-2-phenylethyne (**6d**), reacted with sulfur to give the corresponding stable 1,2-dithietes **7a**—**d** in 46—65% yields. Less hindered alkynes reacted with sulfur to afford 1,4-dithiins and thiophenes as the final products which were derived from the initial products, 1,2-dithietes, via their tautomerization to the corresponding 1,2-dithioxo compounds, while extremely congested alkynes failed to react with sulfur even under forcing conditions. On the other hand, ynamines, a typical electron-rich alkyne, 1-diethylamino-2-phenylthioethyne (**6o**), 1-diethylamino-2-phenylselenoethyne (**6p**), and tetraethylethynediamine (**6q**) were sulfurated under milder conditions to afford resonance-stabilized 1,2-dithioxo compounds **19o**—**q** as the principal products. Mechanism of the formation of 1,2-dithietes, 1,2-dithioxo compounds, and other products is discussed.

In connection with our continuing interest in reactions of elemental sulfur with acetylenic compounds,1) we report here a convenient synthesis of 1,2-dithietes stabilized by buttressing effect and 1,2-dithioxo compounds stabilized by resonance effect by sulfuration of disubstituted alkynes with elemental sulfur.2) 1,2-Dithietes are structurally interesting compounds which possess one carbon–carbon double bond and one disulfide linkage in their strained four-membered ring. Most of them are highly reactive and elude isolation at room temperature. Their facile tautomerization to the corresponding reactive 1,2-dithioxo compounds must be, at least in part, responsible for their instability.3) Thus, the first isolable 1,2-dithiete **1**, whose tautomeric 1,2-dithioxo form is electronically disfavored by strongly electron-withdrawing trifluoromethyl groups, was obtained by sulfuration of highly reactive hexafluoro-2-butyne under flow system.4) Another factor of stabilizing dithietes is buttressing effect, which makes the tautomerization to 1,2-dithioxo compounds unfavorable. Thus, dithietes **2** are prepared by sulfuration of 3,3,7,7-tetramethyl-5-thiacycloheptyne and its 5,5-dioxide derivative whose triple bonds are highly activated by large angle strain.5) Photochemical extrusion of ethylene from a 1,4-benzodithiane derivative also affords a sterically buttressed stable benzodithiete **3**.6) A stable 3,4-di-*t*-butyl-1,2-dithiete **7a** is also prepared in 45% yield by thionation of 2,2,5,5-tetramethyl-4-thioxo-3-hexanone which is obtained in low overall yield in a tedious multistep synthesis.7) An attempt to obtain **7a** directly by thionation of 2,2,5,5-tetramethyl-3,4-hexanedione is unsuccessful.7a) 1,2-Dithioxo compounds, valence tautomers of 1,2-dithietes, are very reactive species and have been usually characterized by trapping reactions.3b,7b,8—10) However, resonance-stabilized or push-pull-stabilized analogs are isolably stable. Compounds **4a**,3b) **4b**,11) **4c**,12) **4d**,13) and **4e**14) and **5**15) belong to these classes (Chart 1).



1

2: X = S, SO$_2$

3

4a: R^1 = R^2 = C$_6$H$_4$NMe$_2$(*p*)
b: R^1 = R^2 = OMe
c: R^1 = R^2 = SMe
d: R^1 = SMe, R^2 = morpholino
e: R^1 = R^2 = NR^2

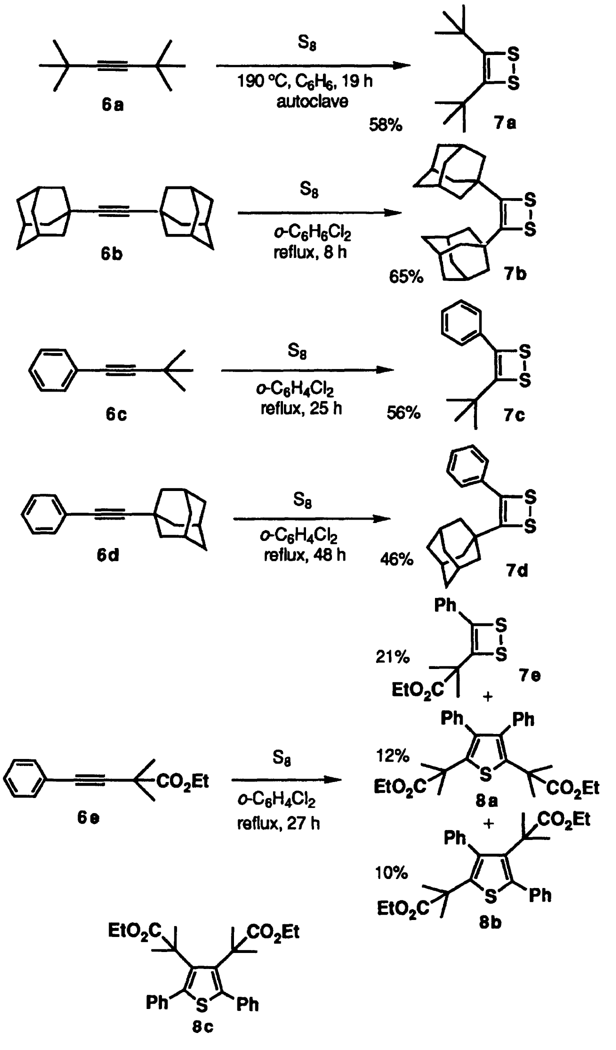
5: R = SR', OR'

Chart 1.

Results and Discussion

We have experienced in the previous study16) that the dithiete **7a** is thermally far stabler than we expected; it is recovered nearly quantitatively after heating in refluxing *o*-dichlorobenzene for many hours. It is also inert to elemental sulfur even under forcing conditions; the expected reaction leading to cyclic polysulfides such as trithiole and pentathiepin derivatives did not take place. These findings prompted us to examine the preparation of **7a** by sulfuration of 2,2,5,5-tetramethyl-3-hexyne (**6a**) with elemental sulfur, the method used for the preparation of the dithietes **1** and **2**.4,5) After many attempts under various conditions, we have found that **7a** is obtained in 58% yield by simple heating of a mixture of **6a** and sulfur in benzene in a stainless steel autoclave at 190°C for 19 h. The present method is far superior to the reported one7) because of the simple experimental procedure, short-step synthesis, better overall yield, and easy availability of **6a** [obtainable from commercially available 1,2-bis(trimethylsilyl)ethyne and *t*-butyl chloride].[17]

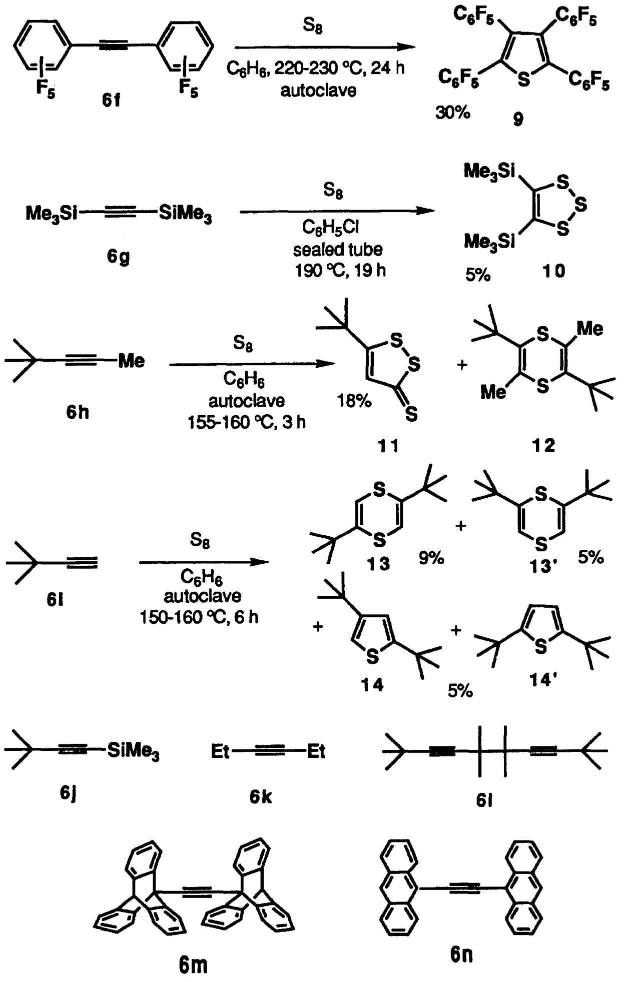
1,2-Di-(1-adamantyl)ethyne (**6b**), also readily obtainable from 1,2-bis(trimethylsilyl)ethyne,[17] is more reactive toward sulfur than **6a** and reacted with it in refluxing *o*-dichlorobenzene for 8 h to give the expected dithiete **7b** in 65% yield as highly thermally stable, nicely crystalline, faintly yellow compound. 3,3-Dimethyl-1-phenyl-1-butyne (**6c**) and 1-(1-adamantyl)-2-phenylethyne (**6d**) were also sulfurated in refluxing *o*-dichlorobenzene to give the expected dithietes **7c** and **7d** in 56 and 46% yields, respectively. Heating a mixture of ethyl 2,2-dimethyl-4-phenyl-3-butynoate (**6e**) and elemental sulfur in refluxing *o*-dichlorobenzene gave the expected dithiete **7e** in 21% yield along with thiophenes **8a** (12%) and **8b** (10%). All of the dithietes **7a**—**e** thus obtained were characterized by spectroscopic means and by elemental analyses or high-resolution mass spectra. In the UV spectra, all of them have weak characteristic absorptions around 340 nm as previously reported with **1**[4] and **7a**.[7] In the ^{13}C NMR spectra, sp^2 carbon signals of the four-membered ring appear in the region of $\delta = 141$—144. Structure discrimination between the thiophene **8a** and its positional isomer **8c** was made by UV spectra. UV spectra of **8a** and 2,5-diethyl-3,4-diphenylthiophene[18] are similar to each other; the absorption maximum of **8a** appears at 236 nm (ε 6205) with a shoulder at 250 nm and that of the latter thiophene at 240 nm (ε 2292) with a shoulder at 256 nm in hexane. The absorption maximum of 3,4-diethyl-2,5-diphenylthiophene[18] in which more effective conjugation between the thiophene and benzene rings takes place appears at 292 nm (ε 1488) in hexane (Scheme 1).



Scheme 1.

The reaction of 1,2-bis(pentafluorophenyl)ethyne (**6f**) with sulfur is sluggish even under forcing conditions. When a mixture of **6f** and sulfur in benzene was heated at 220—230°C for 24 h in an autoclave, the thiophene **9** was obtained in 30% yield, as previously reported,[19] with 46% recovery of **6f**. No dithiete was formed. 1,2-Bis(trimethylsilyl)ethyne (**6g**) reacted with sulfur to give the trithiole **10** as red crystals [$\lambda_{\max}$ 363 (ε 185), 492 (197) nm in hexane] in low yield; no expected dithiete was formed in any amount. The low material balance of this reaction should be ascribed to the silicon-carbon bond cleavage by sulfur, which leads to polymeric tarry materials. 4,4-Dimethyl-2-pentyne (**6h**) reacted with sulfur to give the 1,2-dithiole-3-thione **11** (18%) and 1,4-dithiin **17** (2%). The present reaction may provide a new synthesis of 1,2-dithiole-3-thiones and thus generality of the reaction remains to be investigated. 3,3-Dimethyl-1-butyne (**6i**) reacted with sulfur to give 2,5-di-*t*-butyl-1,4-dithiin (**13**) (9%), 2,6-di-*t*-butyl-1,4-dithiin (**13′**) (5%), and a 4 : 1 mixture of 2,4- and 2,5-di-*t*-butylthiophenes (**14** and **14′**). The reaction of 3,3-dimethyl-1-trimethylsilyl-1-butyne (**6j**) with sulfur gave a complex mixture from which a 3 : 2 mixture of the isomeric thiophenes **14** and **14′** was isolated in very low yield as the only identifiable product. No product carrying trimethylsilyl group was isolated. The sulfuration of a simple alkyne like as 3-hexyne (**6k**) gave a complex mixture from which any pure product could not be isolated. Disappointingly, highly sterically congested alkynes such as **6l**, **6m**, and **6n** failed to react with sulfur because of steric hindrance. The reactions under highly forcing conditions resulted in the formation of tarry materials instead of giving desired 1,2-dithietes (Scheme 2).

The formation of 1,2-dithietes, 1,4-dithiins, and thiophenes described above can be best explained as follows. Heating elemental sulfur (S_8) leads to homolytic S–S bond scission to give diradical sulfur $\cdot SS_6S\cdot$, which then produces a large number of compounds of sulfur including diradical sulfur $\cdot SS_xS\cdot$.[20] The diradical sulfur thus formed would add to the alkynes **6** to give the diradical intermediates **15**. Intramolecular cyclization of **15** with elimination of S_x affords 1,2-dithietes **7**. In the case of alkynes **6e**, **6f**, **6h**, and **6i**, the dithietes **7** undergo ring-opening to give the corresponding 1,2-dithioxo tautomers **16**. Diels–Alder reaction of **16** with



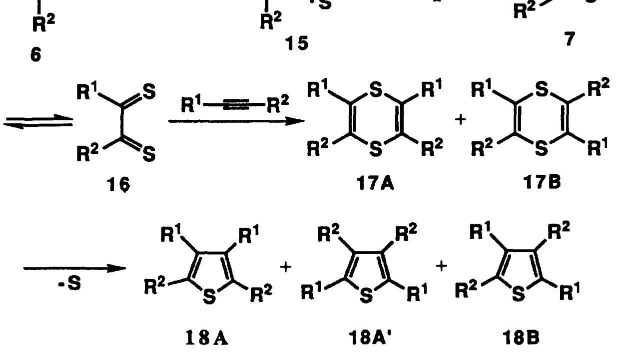
Scheme 2.

the starting alkynes would give rise to the 1,4-dithiins **17A** and/or **17B**. Finally sulfur extrusion of **17A** would afford the thiophenes **18A** and/or **18B** and that of **17B** afford **18B**.[21]

Thermal stability of the dithietes **7a**—**d** should be mostly ascribed to their restricted isomerization to cisoid 1,2-dithioxo tautomers **16** due to buttressing effect by bulky substituents;[22] tautomerization to **16** is sterically unfavorable because two bulky subsituents come nearer during this process due to the decrease of bond angles R^1–C(sp^2)–C(sp^2) and R^2–C–C, and thus the transition state leading to **16** becomes unfavorable by steric repulsion. It is rather surprising that even **7c** and **7d** are highly thermally stable in the dithiete form, as we can see from the reaction conditions under which they were prepared, regardless the fact that tautomerization to the corresponding 1,2-dithioxo compounds would make the conjugation between the phenyl and thioxo groups possible. ^{1}H and ^{13}C NMR analyses of these compounds did not give any sign of the existence of the 1,2-dithioxo tautomers. The formation of **8a** and **8b** from **6e** indicates that the tautomerization of **7e** takes place more easily in refluxing *o*-dichlorobenzene than that of **7a**—**d**. Thus, tautomerization of **7e** followed by Diels–Alder reaction of the resulting 1,2-dithioxo compounds with the starting alkyne **6e** affords two types of adducts **17A** ($R^1=C(CH_3)_2CO_2Et$, $R^2=Ph$) and **17B**. The sole formation of **8** indicates that sulfur extrusion from the adduct of type **17A** takes place selectively to give only less congested **8a**. The formation of **8b** can be explained as the result of sulfur extrusion from the adduct of type **17B**. In fact, heating a mixture of the 1,2-dithiete **7e** and the alkyne **6e** in refluxing *o*-dichlorobenzene for 23 h afforded **8a** and **8b** in 23 and 31%, respectively, with 38% recovery of **7e**. The same explanation may hold for the formation of dithiins **13** and **13′** and thiophenes **14** and **14′** from **6i**. The formation of the dithiole **11** from **6h** indicates that the diradical sulfur $\cdot SS_xS\cdot$ abstracts a methyl hydrogen of **6h** to give the radical (t-BuC≡CCH$_2\cdot$) from which **11** must be finally formed through reaction with sulfur. Therefore, application of the present dithiete synthesis seems to be limited to the alkynes having no α-hydrogen to the triple bond. Nevertheless, the present reaction is very convenient for the preparation of sterically congested 1,2-dithietes and would help to open a new chemistry of 1,2-dithietes which have not been much explored for lack of good synthetic method.

Unfortunately, all attempts to prepare 1,2-diselenetes by reactions of alkynes **6a** and **6b** with elemental selenium were unsucessful, although hexafluoro-2-butyne is known to react with selenium vapor at 750°C to give 3,4-bis(trifluoromethyl)-1,2-diselenete (Scheme 3).[23]

Reactions of elemental sulfur with ynamines, a typical electron-rich alkyne, proceed under milder conditions. Thus, heating a mixture of 1-diethylamino-2-phenylthioethyne (**6o**) and sulfur in refluxing chlorobenzene for 2 h afforded a dithioxo compound, *N*,*N*-diethyl-2-thioxo-2-(phenylthio)ethanethioamide (**19o**), in 74% yield along with diphenyl trisulfide in 20% yield. Similarly, 1-diethylamino-2-phenylselenoethyne (**6p**) was sulfurated in refluxing toluene to give *N*,*N*-diethyl-2-thioxo-2-(phenylseleno)ethanethioamide (**19p**) in 12% yield along with diphenyl diselenide in 80%

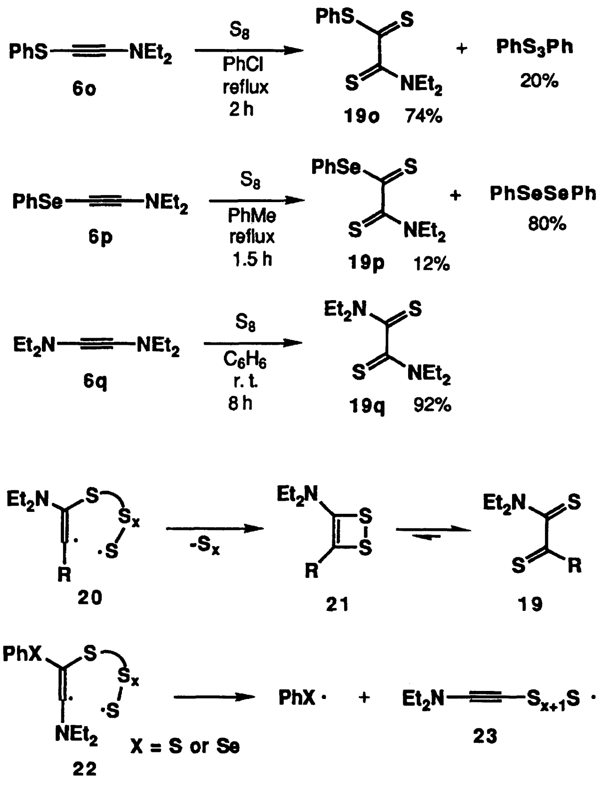


Scheme 3.

yield. Although we have preliminarily reported[2] that tetraethylethynediamine (**6q**) reacted with sulfur at 75°C in chlorobenzene to afford tetraethylethanedithioamide (**19q**) in 69% yield, the reaction occurs even at room temperature for 8 h to give **19q** in 92% yield. In ^{1}H and ^{13}C NMR spectra, two ethyls of the diethylamino group of **19o**—**q** appear nonequivalent because of the restricted rotation about the nitrogen–sp^2 carbon bond.

Also in the present case, diradical intermediates **20**, in which sulfur is attached to the carbon carrying Et_2N group, must be initially formed. Elimination of S_x from **20** would afford dithietes **21**, which then undergo ring-opening to give resonance-stabilized and thus more thermodynamically stable 1,2-dithioxo compounds **19**. The initial formation of diradical intermediates **22**, in which C–S bond is formed between sulfur and the carbon carrying PhX (X = S or Se) group, will explain the formation of diphenyl trisulfide and diphenyl diselenide. The diradicals **22** would expel PhX•, and PhS• thus formed would react with sulfur to give diphenyl trisulfide, while PhSe• undergo dimerization to give diphenyl diselenide. Unfortunately, however, efforts to capture the compounds derived from the radical **23** were unsuccessful (Scheme 4).

Although dithioxo compounds stabilized by resonance effect can be prepared by other methods,[3b,11—15] the present reaction provides a unique synthetic method for this class of compounds.



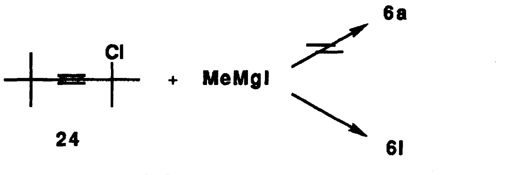
Scheme 4.

Experimental

General. Melting points were determined on a MEL-TEMP capillary tube apparatus and are uncorrected. Both ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q or a Bruker WM-400 spectrometer. Chemical shifts are expressed in parts per million from tetramethylsilane as an internal standard. Mass spectra were determined on a Shimadzu QP-1000 or a JEOL DX-303 spectrometer. High resolution mass spectra were determined on a JEOL DX303 spectrometer. IR spectra were taken on a Hitachi 270-50 spectrometer. UV spectra were recorded on a Shimadzu UV-160A spectrometer. Column chromatography was conducted using E. Merck silica gel 60 (70-230 mesh).

Starting Alkynes. Alkynes **6g**, **6h**, and **6k** are commercial sources. Alkynes **6a** and **6b** were prepared by reaction of **6g** with *t*-butyl chloride and 1-bromoadamantane, respectively.[17] Alkynes, **6c**,[17] **6d**,[17] **6e**,[24] **6f**,[25] **6i**,[26] **6j**,[27] **6m**,[28] and **6n**,[29] were synthesized according to the literature methods. Ynamines, **6o**,[30] **6p**,[31] and **6q**,[32] were also prepared by the literature methods. We could obtain the alkyne **6l** serendipitously. It was reported that the reaction of 2-chloro-2,5,5-trimethyl-3-hexyne (**24**) with methylmagnesium bromide in ether affords the alkyne **6a** in 70% yields.[33] However, when we used methylmagnesium iodide instead of methylmagnesium bromide, we could obtain the coupling product **6l** unexpectedly as the principal product. Thus, methylmagnesium iodide was prepared from 28.7 g (0.20 mol) of methyl iodide and 4.91 g (0.20 mol) of magnesium in ether (ca. 60 cm^3). To this methylmagnesium iodide solution was added a solution of 25.7 g (0.16 mol) of **24** in ether (ca. 50 cm^3) under ice-cooling over a period of 3 h. The mixture was slowly warmed to room temperature and then refluxed for 1 h. The cooled reaction mixture was quenched by addition of 3 M (1 M = 1 mol dm^{-3}) hydrochloric acid (22 cm^3). The deeply colored organic layer due to the formation of iodine was washed with an aqueous solution of $Na_2S_2O_4$ to remove iodine and then with water and dried over Na_2SO_4. The extract turned deep red on evaporation of the ether to give a crystalline residue. The colored residue was dissolved in pentane and washed again with an aqueous solution of $Na_2S_2O_4$ and then with water and dried. The pentane was evaporated and the crystalline residue was rinsed with ethanol to give 8.0 g (72%) of **6l**, mp 109—110°C (lit,[34] mp 112.4—112.7°C) (Scheme 5).

Reaction with 2,2,5,5-Tetramethyl-3-hexyne (6a). A mixture of 2.76 g (20 mmol) of **6a** and 2.56 g (10 mmol as S_8) of sulfur in benzene (100 cm^3) was heated at 190°C for 19 h in a stainless steel autoclave. The resulting mixture was evaporated under reduced pressure. Pentane (ca. 15 cm^3) was added to the residue and the insoluble material (mainly excess sulfur) was removed by filtration. The residue was kept in a refrigerator overnight. The resulting deposit of sulfur was removed by filtration and the filtrate



Scheme 5.

was evaporated. The residue was distilled to give 2.34 g (58%) of 3,4-di-*t*-butyl-1,2-dithiete (**7a**) as pale red liquid, bp 80—82°C/1.4 mmHg (1 mmHg=133.322 Pa) [lit,[7a)] bp 50°C/0.1 mmHg (molecular distillation)].

Reaction with 1,2-Di-(1-adamantyl)ethyne (6b). A mixture of 1.18 g (4 mmol) of **6b** and 0.51 g (2 mmol as S_8) of sulfur in *o*-dichlorobenzene (40 cm^3) was refluxed for 8 h under argon. The mixture was evaporated under reduced pressure. The residue was chromatographed on a column of silica gel (ca. 70 g). Elution with hexane gave unreacted sulfur, a small amount of **6b**, and 0.93 g (65%) of 1,2-di-(1-adamantyl)-1,2-dithiete (**7b**) in this order. **7b**: Faintly yellow leaflets; mp 197—198°C (from hexane); ^{1}H NMR ($CDCl_3$) δ=1.38 (12H, m), 1.53 (12H, d), 1.71 (6H, s); ^{13}C NMR ($CDCl_3$) δ=28.60 (d), 36.45 (t), 38.92 (s), 41.63 (t), 141.93 (s, sp^2 carbon of dithiete ring); MS (EI) *m/z* 358 (M^+), 294, 179, 135 (base peak); IR (KBr) 1555, 1453, 1354, 1313, 1100, 984, 935, 794 cm^{-1}; UV (hexane) λ_{max} 229 (ε 5600), 278 (491), 349 nm (265). Found: C, 73.52; H, 8.55%. Calcd for $C_{22}H_{30}S_2$: C, 73.69; H, 8.42%.

Reaction with 3,3-Dimethyl-1-phenyl-1-butyne (6c). A mixture of 158 mg (1 mmol) of **6c** and 129 mg of sulfur was heated in refluxing *o*-dichlorobenzene (7 cm^3) for 25 h under argon. The mixture was evaporated under reduced pressure. Purification of the residue gave 124 mg (56%) of 3-*t*-butyl-4-phenyl-1,2-dithiete (**7c**): Faintly yellow oil; ^{1}H NMR ($CDCl_3$) δ=1.63 (9H, s), 7.28 (5H,s); ^{13}C NMR ($CDCl_3$) δ=29.85 (q), 37.39 (s), 128.14 (s), 128.49 (d), 128.92 (d), 129.61 (d), 137.07 (s, dithiete ring carbon), 143.83 (s, dithiete ring carbon); MS (EI) *m/z* 222 (M^+), 207, 158, 243; UV (hexane) λ_{max} 233 (ε 4494), 303 (2536), 349 nm (203). Found: *m/z* 222.0549. Calcd for $C_{12}H_{14}S_2$: 222.0537.

Reaction with 1-(1-Adamantyl)-2-phenylethyne (6d). A mixture of 184 mg (0.8 mmol) of **6d** and 100 mg of sulfur was heated in refluxing *o*-dichlorobenzene (10 cm^3) for 2 d under argon. The mixture was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography to give 122 mg (52%) of 3-(1-adamantyl)-4-phenyl-1,2-dithiete (**7d**); mp 81—82°C, yellow crystals (from hexane); ^{1}H NMR ($CDCl_3$) δ=1.65 (6H, m), 1.81 (6H, d), 1.94 (3H, s), 7.28—7.39 (5H, m); ^{13}C NMR 28.23 (d), 36.36 (t), 49.42 (s), 41.67 (t), 127.62 (s), 127.91 (d), 127.97 (d), 128.97 (d), 137.12 (s, dithiete ring carbon), 144.28 (s, dithiete ring carbon); MS (EI) *m/z* 300 (M^+), 236, 179, 135 (base peak); UV (hexane) λ_{max} 233 (ε 5357), 305 (3132), 345 nm (171). Found: C, 71.95; H, 6.71% Calcd for $C_{18}H_{20}S_2$: C, 71.86; H, 6.71%.

Reaction with Ethyl 2,2-Dimethyl-4-phenyl-3-butynoate (6e). A mixture of 1.08 g (5 mmol) of **6e** and 0.64 g of sulfur was heated in refluxing *o*-dichlorobenzene (30 cm^3) for 27 h under argon. The mixture was evaporated and the residue was purified by silica-gel column chromatography [elution with CCl_4/benzene (=1/1) and then with CH_2Cl_2/benzene (=2/1)] to give 289 mg (21%) of 3-(1-methyl-1-ethoxycarbonylethyl)-4-phenyl-1,2-dithiete (**7e**), 133 mg (12%) of 2,5-bis(1-methyl-1-ethoxycarbonylethyl)-3,4-diphenylthiophene (**8a**), and 110 mg (10%) of 2,4-bis(1-methyl-1-ethoxycarbonylethyl)-3,5-diphenylthiophene (**8b**).

7e: Viscous reddish brown oil; ^{1}H NMR ($CDCl_3$) δ= 1.13 (3H, t), 1.44 (6H, s), 4.02 (2H, q), 7.34—7.25 (5H, m); ^{13}C NMR ($CDCl_3$) δ=13.89 (q), 25.30 (q), 47.05 (s), 61.41 (t), 127.51 (d), 128.22 (d), 128.30 (d), 130.44 (s), 135.27 (s, dithiete ring carbon), 135.68 (s, dithiete ring carbon), 174.58 (s, ester carbonyl); MS (EI) *m/z* 280 (M^+), 252, 234, 207 (base peak), 175, 143, 128, 121; UV (hexane) λ_{max} 290 (ε 2055), 302 (2015), ca. 345 nm (sh) (980). Found: *m/z* 280.0592. Calcd for $C_{14}H_{16}O_2S_2$: M, 280.0610.

8a: Mp 113—113.5°C (from hexane); ^{1}H NMR ($CDCl_3$) δ=1.11 (6H, t), 1.53 (12H, s), 3.79 (4H, q), 7.04—7.05 (6H, m), 6.88—6.91 (4H, m); ^{13}C NMR ($CDCl_3$) δ=13.89 (q), 28.66 (q), 44.83 (s), 60.82 (t), 126.65 (d), 127.03 (d), 130.83 (d), 136.83 (s), 140.15 (s), 140.29 (s), 175.65 (s); UV (hexane) λ_{max} 213 (ε 7137), 236 (6205), 250 nm (sh) (4328). Found: C, 72.02; H, 6.86%. Calcd for $C_{28}H_{32}O_4S$: C, 72.38; H, 6.94%.

8b: Mp 112—113°C (from hexane); ^{1}H NMR ($CDCl_3$) δ=1.01 (3H, t), 1.12 (3H, t), 1.17 (6H, s), 1.44 (6H, s), 3.55 (2H, q), 3.84 (2H, q), 7.46—7.48 (2H, m), 7.30—7.36 (6H, m), 7.19—7.22 (2H, m); ^{13}C NMR ($CDCl_3$) δ=13.59 (q), 13.77 (q), 28.30 (q), 28.86 (q), 44.51 (s), 46.41 (s), 60.12 (t), 60.65 (t), 126.98 (d), 127.46 (d), 127.66 (d), 127.79 (d), 130.94 (d), 132.73 (d), 135.01 (s), 136.04 (s), 136.10 (s), 138.62 (s), 139.76 (s), 144.02 (s), 175.29 (s), 176.21 (s). Found: C, 72.34; H, 6.89% Calcd for $C_{28}H_{32}O_4S$: C, 72.38; H, 6.94%. 3,4-Diethyl-2,5-diphenyl- and 2,5-diethyl-3,4-diphenylthiophenes, which were used for comparision of UV spectra with **8a**, were previously prepared in our laboratories.[18)]

Reaction of 7e with 6e. A mixture of 100 mg (0.36 mmol) of **7e** and 78 mg (0.36 mmol) of **6e** in *o*-dichlorobenzene (5 cm^3) was heated under reflux for 23 h under argon. The mixture was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography to give 60 mg of a 1 : 1.7 mixture of **7e** and **6e**, 38 mg (23%) of **8a**, and 52 mg (31%) of **8b**.

Reaction with 1,2-Bis(pentafluorophenyl)ethyne (6f). A mixture of 143 mg (0.4 mmol) of **6f** and 51 mg of sulfur in benzene (40 cm^3) was heated in a stainless steel autoclave for 24 h at 220—230°C. The mixture was evaporated and the residue was chromatographed on a column of silica gel. Elution with hexane gave sulfur, 65 mg (48%) of **6f**, and then 45 mg (30%) of 2,3,4,5-tetrakis(pentafluorophenyl)thiophene (**9**); mp 184—186°C (lit,[19)] mp 180—180.5°C); MS (EI) *m/z* 748 (M^+), 374 (M^{2+}), 327, 211 (base peak); ^{13}C NMR ($CDCl_3$) δ=106.36 (m), 107.89 (m), 128.83 (s, thiophene ring carbon), 130.07 (s, thiophene ring carbon), 136.21 (m), 136.60 (m), 138.74 (m), 139.15 (m), 140.54 (m), 141.09 (m), 142.83 (m), 143.20 (m), 143.65 (m), 145.34 (m), 147.75 (m).

Reaction with 1,2-Bis(trimethylsilyl)ethyne (6g). A mixture of 340 mg (2 mmol) of **6g** and 256 mg of sulfur in chlorobenzene (10 cm^3) was heated in a sealed glass tube at 190°C for 13 h. The mixture was evaporated and the residue was chromatographed on a column of silica gel. Elution with hexane gave 24 mg (5%) of 4,5-bis(trimethylsilyl)trithiole (**10**): Red crystals, mp 33.5—34.5°C; ^{1}H NMR ($CDCl_3$) δ= 0.34 (s, 18H); ^{13}C NMR ($CDCl_3$) δ=1.64 (q), 145.08; MS (EI) *m/z* 266 (M^+), 202, 187, 73 (base peak); UV (hexane) λ_{max} 249 (ε 1960), 279 (1937), 363 (185), 492 nm (197). Found: *m/z* 266.0110. Calcd for $C_8H_{18}Si_2S_3$: M, 266.0109.

Reaction with 4,4-Dimethyl-2-pentyne (6h). A mixture of 960 mg (10 mmol) of **6h** and 1.28 g of sulfur in benzene (50 ml) was heated at 155—160°C for 3 h in a stainless steel autoclave. The mixture was evaporated and the residue was chromatographed on a column of silica gel. Elution with hexane gave sulfur and then 27 mg (2%) of 2,5-*t*-butyl-3,6-dimethyl-1,4-dithiin (**12**) and then elution with carbon tetrachloride gave 351 mg (18%) of 5-*t*-butyl-1,2-dithiole-3-thione (**11**): Mp 69—70°C (lit,[35] mp 69—69.5°C); ^{1}H NMR (CDCl$_3$) δ=1.44 (9H, s), 7.14 (1H, s); ^{13}C NMR (CDCl$_3$) δ=31.35 (q), 38.30 (s), 136.57 (d), 188.48 (s), 216.52 (s).

13: Mp 41—43°C; ^{1}H NMR (CDCl$_3$) δ=1.30 (18H, s), 2.30 (6H, s); ^{13}C NMR (CDCl$_3$) δ=22.59 (q), 30.91 (q), 38.75 (s), 130.81 (s), 146.91 (s); MS (EI) *m/z* 256 (M$^+$), 200, 185. Found: *m/z* 256.1320. Calcd for $C_{14}H_{24}S_2$: M, 256.1310.

Reaction with 3,3-Dimethyl-1-butyne (6i). A mixture of 246 mg (3 mmol) of **6i** and 384 mg of sulfur in benzene (30 ml) was heated at 150—160°C for 6 h in a stainless steel autoclave. The mixture was evaporated and the residue was chromatographed on a column of silica gel. Elution with hexane gave sulfur, 14 mg (5%) of a 4 : 1 mixture of 2,4- and 2,5-di-*t*-butylthiophenes (**14** and **14′**), 30 mg (9%) of 2,5-di-*t*-butyl-1,4-dithiin (**13**), and 16 mg (5%) of 2,6-di-*t*-butyl-1,4-dithiin (**13′**), in this order. Structures of **13**,[36] **13′**,[36] **14**[37] were determined by comparison of their spectroscopic properties with those of authentic samples which had been previously prepared in our laboratories.

Reaction with 3,3-Dimethyl-1-trimethylsilyl-1-butyne (6j). Heating a mixture of 1.00 g (6.5 mmol) of **6j** and 831 mg of sulfur in benzene (40 cm^3) at 190°C for 17.5 h in a stainless steel autoclave gave 30 mg (5%) of a 3 : 2 mixture of thiophenes **14** and **14′** after purification by silica-gel column chromatography.

Reactions with Alkynes 6l, 6m, and 6n. Reactions of these alkynes with sulfur were examined under a wide variety of conditions. However, these alkynes did not react with sulfur under the conditions which the alkynes described above reacted with sulfur, and the application of more forcing conditions gave only tarry materials.

Reaction with 1-Diethylamino-2-phenylthioethyne (6o). A mixture of 410 mg (2 mmol) of **6o** and 256 mg of sulfur in chlorobenzene (30 ml) was heated under reflux for 2 h under argon. After removal of the solvent, the residue was chromatographed on a column of silica gel. The column was first eluted with hexane to give unreacted sulfur and 50 mg (20%) of diphenyl trisulfide:[38] yellow oil; [MS (EI) *m/z* 250 (M$^+$), 218, 186, 154] and then eluted with benzene to give 396 mg (74%) of *N*,*N*-diethyl-2-thioxo-2-(phenylthio)ethanethioamide (**19o**): Mp 47—49°C (from hexane), reddish orange crystals; ^{1}H NMR (CDCl$_3$) δ=1.08 (3H, t), 1.29 (3H, t), 3.65 (2H, q), 3.87 (2H, q), 7.48 (5H, m); ^{13}C NMR (CDCl$_3$) δ=10.71 (q), 13.19 (q), 44.86 (t), 44.71 (t), 129.37 (s), 129.61 (d), 130.89 (d), 135.17 (d), 195.44 (s, C=S), 226.34 (s, C=S) (two ethyls are nonequivalent because of restricted rotation); MS (EI) *m/z* 269 (M$^+$), 254, 205, 88 (base peak); $\lambda_{\max}$ (hexane) 217 (ε 10050), 271 (10560), 318 (6350), 349 (4590), 396 (2520), 495 nm (280). Found: C, 53.41; H, 5.68%. Calcd for $C_{12}H_{15}NS_3$: C, 53.49; H, 5.61%.

Reaction with 1-Diethylamino-2-phenylselenoethyne (6p). A mixture of 533 mg (2.1 mmol) of **6p** and 271 mg of sulfur in toluene (30 cm^3) was heated under reflux for 1.5 h under argon. After removal of the solvent, the residue was chromatographed on a column of silica gel. The column was first eluted with hexane to remove the excess sulfur, then eluted with benzene/hexane (=1/1) to give 275 mg (83%) of diphenyl diselenide, mp 57—57.5°C [mp of the commercial product (Aldrich), 60—62°C], and finally eluted with benzene to give 78 mg (12%) of *N*,*N*-diethyl-2-thioxo-2-(phenylseleno)ethanethioamide (**19p**): Mp 72—73°C (from hexane), dark red plates; ^{1}H NMR (CDCl$_3$) δ=0.98 (3H, t), 1.25 (3H, t), 3.60 (2H, q), 3.79 (2H, q), 7.46 (3H, m), 7.63 (2H, m); ^{13}C NMR (CDCl$_3$) δ=10.56, 12.93, 44.69, 47.33, 129.05, 129.61, 130.22, 136.40, 197.08 (C=S), 229.44 (C=S); IR (KBr) 1516, 1462, 1441, 1283, 1227, 1179, 1135, 1016, 992, 884, 740, 686 cm^{-1}; MS (EI) *m/z* 319, 317, 315 (M$^+$), 205, 160 (base peak), 128, 115. Found: *m/z* 317.9828. Calcd for $C_{12}H_{15}NS_2Se$: M, 317.9890.

Reaction with Tetraethylethynediamine (6q). a) At 75°C. A mixture of 112 mg (0.67 mmol) of **6q** and 154 mg of sulfur in chlorobenzene (18 cm^3) was heated at 75°C for 0.5 h under argon. The mixture was evaporated under reduced pressure and the residue was chromatographed on a column of silica gel. The column was first eluted with hexane to remove the excess sulfur and then eluted with benzene/ethyl acetate (=95/5) to give 107 mg (69%) of tetraethylethanedithioamide (**19q**): Mp 85—86°C (lit,[14b] mp 88—90°C); ^{13}C NMR (CDCl$_3$) δ=10.45 (q), 12.47 (q), 43.92 (t), 47.41 (t), 192.77 (s, C=S).

b) At Room Temperature. A mixture of 351 mg (2.1 mmol) of **6q** and 275 mg of sulfur in benzene (30 cm^3) was stirred for 8 h at room temperature under argon. Purification of the mixture by silica-gel column chromatography gave 448 mg (92%) of **19q**.

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