Registry No. **1a**, 3555-94-0; **1b**, 1520-22-5; **2**, 4231-35-0; **3a**, 82639-27-8; **3b**, 82639-29-0; **4a**, 82639-26-7; **4b**, 82639-30-3; **5**, 82639-25-6; (*E*)-**6**, 82639-31-4; (*Z*)-**6**, 82639-32-5; **7**, 82639-33-6; **8**, 39273-03-5; **9**, 35774-60-8; CH_2=CHNHC(S)$CHCH_3CONEt_2$, 82639-28-9; 2-bromoethyl isothiocyanate, 1483-41-6; *N*,*N*-diethylpropanamide, 1114-51-8.

Substituent Dependence of the Selectivity in the Cycloadditions of Vinylketenimines with Thiobenzophenone. 1,2- and 1,4-Addition Pathways

Alessandro Dondoni*

Laboratorio di Chimica Organica, Facoltà di Scienze, Università, Ferrara, Italy

Arturo Battaglia and Patrizia Giorgianni

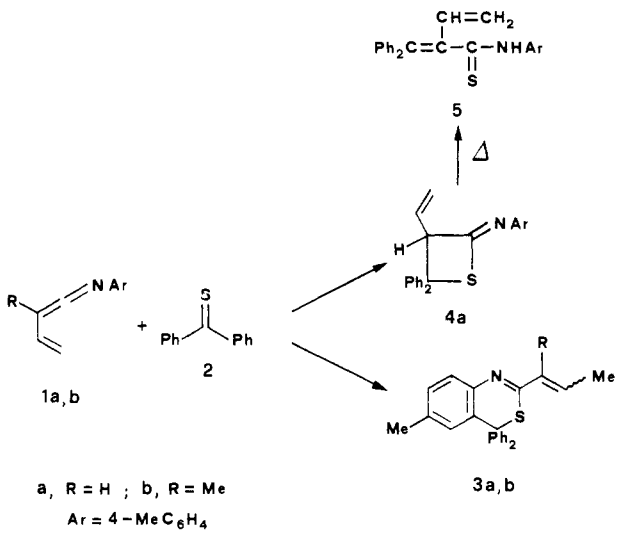
Istituto dei Composti del Carbonio Contenenti Eteroatomi, Consiglio Nazionale delle Ricerche, Ozzano Emilia, Italy

Received April 1, 1982

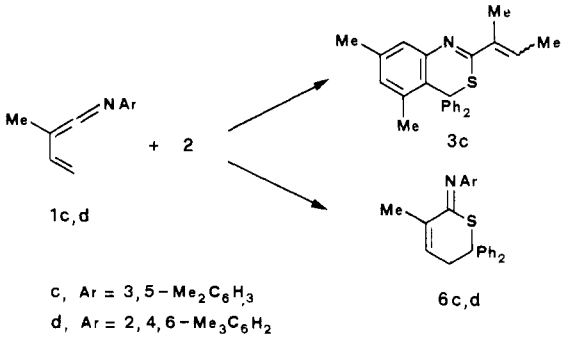
We recently reported[1] two modes of cycloaddition between thiobenzophenones and *C*-methyl and *C*-phenylketenimines, namely, 1,2-cycloaddition of the C=S bond of the thione across the cumulative C=C bond to give 2-iminothietanes and 1,4-cycloaddition across the C=N and one C=C bond of the *N*-aryl group of the cumulene to give 4*H*-3,1-benzothiazines. Another mode of cycloaddition which involves an unsaturated functionality flanking the carbon of the cumulene has been observed[2] with *C*-vinylketenimines and we report here a full account on the selectivity of their reactions with thiobenzophenone. We are investigating[3] the reactivity of other vinylheterocumulenes as a mechanistic probe of cumulene cycloadditions as well as a source of 1,3-diene equivalents for hetero-Diels–Alder reactions.

Four substituted *C*-vinylketenimines **1** were employed for the purposes of the present work, all compounds being stable and readily accessible by conventional preparative methods. Treatment of the C-monosubstituted derivative *N*-*p*-tolylvinylketenimine (**1a**), generated in situ from the corresponding amide by the triphenylphosphine dibromide–triethylamine method, with thiobenzophenone (**2**) at room temperature (Scheme I) gave a mixture (TLC) of the 4*H*-3,1-benzothiazine **3a** and 2-iminothietane **4a**. The presence of the latter adduct in the crude reaction mixture was inferred[1] from a singlet in the ^{1}H NMR spectrum at 5.5 ppm and a strong IR band at 1675 cm^{-1}. When the mixture was heated at 45 °C for 2 days, these signals disappeared and the α,β-unsaturated thioamide **5** (53%) together with the 4*H*-3,1-benzothiazine **3a** (21%) were isolated and identified through their spectroscopic characteristics. If it is accepted that the product distribution is under kinetic control as shown for other ketenimine–thioketone cycloadditions[1] and that the 2-iminothietane **4a** rearranges on heating exclusively to the thioamide **5**, the larger amount of the latter with respect to the benzothiazine **3a** (2.5:1 ratio) indicates the preference by the C=S bond of thioketone **2** for 1,2-cycloaddition across the C=C bond of the cumulative system of **1a** over the *N*-aryl 1,4-cycloaddition.

Scheme I



Scheme II



On the other hand, treatment the C-disubstituted derivative vinylmethylketenimine **1b** with **2** gave as a single product the 1,4-cycloadduct 4*H*-3,1-benzothiazine **3b** in ca. 80% yield (Scheme I). These results parallel our previous finding on the selectivity of *C*-methyl- and *C*-phenylketenimine–thioketone cycloadditions[1] where monosubstituted derivatives reacted according to the 1,2-cycloaddition mode whereas disubstituted compounds preferred the *N*-aryl 1,4-cycloaddition process. As already suggested, this variation of selectivity may be related to the inhibition by steric factors of the 1,2-cycloaddition which on the other hand should be favored by electronic effects.

The *N*-aryl 1,4-cycloaddition of thioketone **2** to ketenimines **1a** and **1b** indicates identical site selectivity as in the reaction of **1b** with (diethylamino)phenylacetylene,[4] a typical electron-rich dienophile, thus suggesting that the C=S bond of the thione **2** behaves as the electron-donor partner toward the heterodiene system C=N—C=C of **1a** and **1b**. However, this selectivity was substantially reduced by *m*-methyl groups in the *N*-aryl ring. Thus ketenimine **1c** with thioketone **2** (Scheme II) gave both *N*-aryl 1,4-cycloaddition to the corresponding 4*H*-3,1-benzothiazine

(1) (a) Dondoni, A.; Battaglia, A.; Giorgianni, P.; Gilli, G.; Sacerdoti, M. *J. Chem. Soc., Chem. Commun.* **1977**, 43. (b) Dondoni, A.; Battaglia, A.; Giorgianni, P.; *J. Org. Chem.* **1980**, *45*, 3766. (c) Dondoni, A.; Battaglia, A.; Bernardi, F.; Giorgianni, P. *Ibid.* **1980**, *45*, 3773. (d) Bernardi, F.; Bottoni, A.; Battaglia, A.; Distefano, G.; Dondoni, A. *Z. Naturforsch., A* **1980**, *35*, 521.

(2) A preliminary account of this work has been presented at the 6th Colloque de Chimie Heterocyclique, Mulhouse, France, 1979, and has been reported in the form of a review paper: Dondoni, A. *Heterocycles* **1980**, *14*, 1547.

(3) Dondoni, A.; Kniezo, L.; Medici, A. *J. Org. Chem.*, previous paper in this issue.

(4) The indicated ynamine gives *N*-aryl 1,4-cycloaddition to **1b**, whereas the electron-poor dienophile dimethyl acetylenedicarboxylate gives *C*-vinyl 1,4-cycloaddition: Ghosez, L.; Sonveaux, E. *J. Am. Chem. Soc.* **1973**, *95*, 5417.

0022-3263/82/1947-3998$01.25/0

3c (45%) and *C*-vinyl 1,4-cycloaddition to the six-membered-ring adduct 2-iminothiacyclohexene derivative **6c** (24%), a sulfur heterocycle hitherto unreported which showed consistent NMR data and a strong IR absorption at 1580 cm^{-1} for the C=N group. The mass spectrum of **6c** showed, in addition to M^+ at *m/e* 383, a fragment at *m/e* 220 corresponding to (M^+ – ArNCS), which supports the assigned regiochemistry. The 2:1 ratio between adducts **3c** and **6c** indicated that the *N*-aryl 1,4-cycloaddition was the lower energy pathway between ketenimine **1c** and thioketone **2**. However, when the two ortho positions of the *N*-aryl ring of the ketenimine were blocked by methyl groups, *C*-vinyl 1,4-cycloaddition occurred selectively. Thus thioketone **2** added to *N*-mesityl derivative **1d** (Scheme II) to give the 2-iminothiacyclohexene **6d** as an adduct in ca. 86% yield.

The above results indicate that *N*-arylvinylketenimines **1** can undergo cycloaddition by thiobenzophenone (**2**) in three different modes: viz., 1,2-addition across the C=C bond of the cumulative system, 1,4-addition involving the cumulene C=N and one C=C bond of the *N*-aryl group, 1,4-addition involving the cumulene C=C bond and the *C*-vinyl group. 1,2-Cycloaddition is favored in the C-monosubstituted derivative **1a** and totally inhibited in the C-disubstituted derivatives **1b–d**, while, other things being equal, the *N*-aryl 1,4-cycloaddition is preferred over the *C*-vinyl 1,4-reaction (see compound **1b**). These results provide new information about the reactivity of ketenimines with thioketones but still leave undefined the electronic factors which direct the choice of the site and peri selectivity in their cycloadditions. Nevertheless, the reactions of vinylketenimines **1** enlarge the synthetic value of ketenimine–thioketone cycloadditions since they provide a direct entry into a class of sulfur heterocycles, viz., thiacyclohexenimines **6**, which can be tested as synthetic intermediates for annulation reactions as well as precursors of the corresponding carbonyl derivatives, viz., thiacyclohexenones, which, on the other hand, do not form from cycloaddition of thioketones to vinylketenes.[5]

Experimental Section

NMR spectra were recorded on an 80-MHz Varian EM 390 spectrometer in the indicated solvent, and all chemical shifts are reported in parts per million (δ) downfield from Me_4Si as the internal standard. IR spectra were determined on a Perkin-Elmer 257 grating spectrometer. Low-resolution mass spectra were recorded at an ionizing voltage of 70 eV on a Varian spectrometer. Analytical TLC was done on E. Merck silica gel 60 plates whereas column chromatography used E. Merck silica gel 60 (70–230 mesh).

Materials. All solvents were purified by standard methods before use.[6] Thiobenzophenone (**2**) was prepared by the literature procedure.[1] Vinylketenimines **1a–c** were obtained from the corresponding amides[7] **7** by a slight modification[1] of the Ph_3P–Br_2–Et_3N method.[8] *N*-*p*-Tolylvinylketenimine (**1a**), whose tendency to polymerize on distillation prevented its isolation and purification, was generated in situ, and the purity (80–85%) was determined by ^1H NMR as described:[1] yellow oil; IR(CCl_4) 2010 cm^{-1}; ^1H NMR (CCl_4) δ 2.33 (s, 3 H, CH_3), 4.63–5.13 (m, 2 H, CH_2=CH, and 1 H, CH=C=N), 5.93–6.4 (m, 1 H, CH=CH_2), 7.12 (s, 4 H, arom). *N*-*p*-Tolylvinylmethylketenimine[4] (**1b**) showed the following: bp 65 °C (0.1 mmHg); IR (CCl_4) 2020 cm^{-1}; ^1H NMR (CCl_4) δ 1.85 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 4.82 (d, 1 H, CH_2=CH), 4.86 (d, 1 H, CH_2=CH), 6.38 (dd, 1 H, CH=CH_2), 7.1 (s, 4 H, arom). *N*-(3,5-Dimethylphenyl)vinylmethylketenimine[1d] (**1c**) showed the following: bp 70 °C (0.1 mmHg); IR (CCl_4) 2020 cm^{-1}; ^1H NMR (CCl_4) δ 1.87 (s, 3 H, CH_3), 2.30 (s, 6 H, CH_3), 4.83 (d, 1 H, CH_2=CH), 4.87 (d, 1 H, CH_2=CH), 6.38 (dd, 1 H, CH=CH_2), 6.82 (s, 3 H, arom). *N*-Mesitylvinylmethylketenimine (**1d**) was generated in situ from equivalent amounts of the appropriate imidoyl chloride[9] and potassium *tert*-butoxide. After rapid addition of the imidoyl chloride in THF to a stirred solution of *t*-BuOK in THF at 0 °C, filtration of the precipitate and removal of the solvent under reduced pressure at low temperature (ca. 5 °C) gave the ketenimine **1d** (85–90% purity) showing the following: oil; IR (CCl_4) 2020 cm^{-1}; ^1H NMR (CCl_4) δ 1.80 (s, 3 H, CH_3), 2.22 (s, 3 H, CH_3), 2.24 (s, 6 H, CH_3), 4.72 (d, 1 H, CH_2=CH), 4.74 (d, 1 H, CH_2=CH), 6.38 (dd, 1 H, CH=CH_2), 6.75 (s, 2 H, arom).

Reactions between Vinylketenimines 1 and Thiobenzophenone (2). The general operative conditions for the mixing of the reactants were as described.[1] Details on each reaction and the characteristics of the products are given below.

Reaction of *N*-*p*-Tolylvinylketenimine (1a). Ketenimine **1a** (0.66 g, 4.2 mmol) and thione **2** (0.77 g, 3.9 mmol) in 10 mL of CCl_4 were allowed to react at 30 °C for 2 days. The reaction mixture was examined for detection of products: TLC (silica; CH_2Cl_2–pentane, 1:2), a spot with R_f 0.60 corresponding to benzothiazine **3a** and a spot with R_f 0.50; IR (CCl_4) 1675 (vs) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.5. The latter spot and the IR and NMR signals which were attributed to the 2-iminothietane **4a** were no longer detectable after heating of the reaction mixture at ca. 50 °C for 2 days. After evaporation of the solvent under reduced pressure, the residue was rapidly eluted (CH_2Cl_2) through a 3-cm-long column of silica to give, in the order of elution, a mixture of benzothiazine **3a** and benzophenone and pure thioacrylamide **5**. High-pressure column chromatography (silica, CH_2Cl_2) allowed the separation of **3a** from the ketone. Yields and characteristics of adducts are as follows.

(a) 2-(1-Propenyl)-4,4-diphenyl-6-methyl-4*H*-3,1-benzothiazine (3a): 0.30 g (0.84 mmol, 21.7%); mp 160–162 °C (from $CHCl_3$–pentane); IR (CCl_4, C_2Cl_2, CS_2) 1650, 1550, 1485 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84 (d, 3 H, CH_3, J = 7.4 Hz), 2.23 (s, 3 H, CH_3), 6.2–6.8 (m, 2 H, =CH), 6.85–7.50 (br s, 13 H, arom); ^{13}C NMR ($CDCl_3$) δ 18.74 and 21.57 (q, CH_3), 59.69 (s, CPh_2), 137.02, 142.68, 143.0 (s, arom), 158.99 (s, C=N); mass spectrum, *m/e* 355 (M^+).

Anal. Calcd for $C_{24}H_{21}NS$: C, 81.09; H, 5.95; N, 3.94. Found: C, 80.92; H, 5.93; N, 3.99.

(b) *N*-*p*-Tolyl-2-vinyl-3,3-diphenylthioacrylamide (5): 0.78 g (2.2 mmol, 56%); mp 180–183 °C (from pentane–ethyl acetate); IR (CCl_4, C_2Cl_4, CS_2) 3390 3360, 1350, 1090 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (s, 3 H, CH_3), 5.25–5.87 (m, 2 H, CH=CH_2), 6.4–6.72 (m, 1 H, CH=CH_2), 6.75–7.6 (m, 14 H, arom), 8.72–8.92 and 9.47–9.67 (br, 1 H, NH); mass spectrum, *m/e* 355 (M^+), 323 (M^+ – S) 249 (M^+ – TolNH).

Anal. Calcd for $C_{24}H_{21}NS$: C, 81.09; H, 5.95; N, 3.94. Found: C, 81.20; H, 5.89; N, 3.87.

Reaction of *N*-*p*-Tolylvinylmethylketenimine (1b). Ketenimine **1b** (0.59 g, 3.5 mmol) was reacted with thioketone **2** (0.68 g, 3.5 mmol) in 10 mL of CCl_4 at 30 °C for 5 days. Evaporation of the solvent and addition of pentane to the residue allowed the isolation of **2-(1-methyl-1-propenyl)-4,4-diphenyl-6-methyl-4*H*-3,1-benzothiazine (3b)**: 1 g (2.7 mmol, 79%); mp 145–153 °C dec (from methanol); IR (CCl_4) 1550 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) δ 1.82 (d, 3 H, CH_3, J = 7.2 Hz), 1.98 (br s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 6.52 (br s, 1 H, arom), 6.70 (q, 1 H, =CH, J = 7.2 Hz), 7.22–7.44 (m, 13 H, arom); ^{13}C NMR ($CDCl_3$) δ 13.91, 15.3, 21.7 (q, CH_3), 59.92 (s, CPh_2), 161.6 (s, C=N); mass spectrum, *m/e* 369 (M^+).

(5) The reaction of vinylmethylketene and **2** gives a thietan-2-one derivative by addition of C=S of the thione across the C=C bond of the cumulative system.

(6) Weissberger, A. "Technique of Organic Chemistry"; Interscience: New York, 1955; Vol. VII.

(7) Amides **7**, CH_2=CHCHRC(O)NHAr, were prepared by conventional methods from the appropriate 3-butenoic acid and substituted anilines. All compounds showed a strong absorption at ca. 1670 cm^{-1} and were crystallized from benzene–petroleum ether: **7a** (R = H, Ar = 4-Me-C_6H_4) from 3-butenoic acid and *p*-toluidine, mp 75–77 °C; **7b** (R = Me, Ar = 4-Me-C_6H_4) from 2-methyl-3-butenoic acid (MBA) and *p*-toluidine, mp 70–72 °C; **7c** (R = Me, Ar = 3,5-$Me_2C_6H_3$) from MBA and 3,5-dimethylaniline, mp 75–76 °C; **7d** (R = Me, Ar = 2,4,6-$Me_3C_6H_2$) from MBA and 2,4,6-trimethylaniline, mp 131–133 °C.

(8) Bestmann, H. J.; Lienert, J.; Mott, L. *Justus Liebigs Ann. Chem.* **1968**, *718*, 24.

(9) This was obtained by chlorination of the amide (**7d**) according to the literature procedure: Stevens, C. L.; French, J. C. *J. Am. Chem. Soc.* **1953**, *76*, 4398.

Anal. Calcd for $C_{25}H_{23}NS$: C, 81.26; H, 6.27; N, 3.79. Found: C, 81.31; H, 6.20; N, 3.83.

Reaction of *N*-(3,5-Dimethylphenyl)vinylmethylketenimine (1c). Ketenimine **1c** (0.80 g, 4.3 mmol) and thioketone **2** (0.9 g, 4.6 mmol) in 10 mL of CCl_4 were allowed to react at room temperature for 35 h. After evaporation of the solvent, column chromatography of the residue (silica; benzene–*n*-pentane, 7:3) gave the following.

(a) 2-(1-Methyl-1-propenyl)-4,4-diphenyl-5,7-dimethyl-4*H*-3,1-benzothiazine (3c): 0.77 g (2.01 mmol, 45%); mp 135–137 °C (from methanol); IR (CCl_4) 1550 cm^{-1}; ^1H NMR δ 1.47 (s, 3 H, CH_3), 1.79 (d, 3 H, CH_3, J = 8.1 Hz), 1.97 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 6.67 (q, 1 H, =CH, J = 8.1 Hz), 6.86 (br, 2 H, arom), 7.20–7.50 (br, 10 H, arom); ^{13}C NMR ($CDCl_3$) δ 13.11, 14.85, 20.61, 23.64 (q, CH_3), 60.90 (s, CPh_2), 136.36, 136.91, 137.28, 142.91, 146.28 (s, arom), 160.8 (s, C=N); mass spectrum, m/e 383 (M^+).

Anal. Calcd for $C_{26}H_{25}NS$: C, 81.42; H, 6.57; N, 3.65. Found: C, 81.53; H, 6.52; N, 3.69.

(b) 3-Methyl-6,6-diphenyl-2-[(3,5-dimethylphenyl)imino]-1-thiacyclohex-3-ene (6c): 0.42 g (1.1 mmol, 24%); mp 186–189 °C (from methanol); IR (CCl_4) 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.95 (d, 3 H, CH_3, J = 1.4 Hz), 2.3 (s, 6 H, CH_3), 3.45 (dd, 2 H, CH_2, J = 5.2, 1.8 Hz), 6.25 (m, 1 H, =CH, J = 5.2, 1.4 Hz), 6.55 (s, 2 H, arom), 6.77 (s, 1 H, arom), 7.32 (m, 10 H, arom); ^{13}C NMR ($CDCl_3$) δ 19.93 (q, CH_3), 21.36 (q, 2 CH_3), 38.14 (t, CH_2), 58.28 (s, CPh_2), 134.55, 138.4, 144.35, 150.57 (s, arom), 183.25 (s, C=N); mass spectrum, m/e 383 (M^+), 220 (M^+ – ArNCS).

Anal. Calcd for $C_{26}H_{25}NS$: C, 81.42; H, 6.57; N, 3.65. Found: C, 81.72; H, 6.47; N, 3.72.

Reaction of *N*-Mesitylvinylmethylketenimine (1d). A solution of crude ketenimine **1d** (1.11 mmol) in 10 mL of CCl_4 prepared in situ from the corresponding imidoyl chloride[9] as described above was reacted with a twofold molar excess of thione **2** (0.4 g, 2.2 mmol) at room temperature for 14 h. From the IR spectrum of the solution the ketenimine **1d** was no longer detectable, whereas from the UV spectrum it appeared that 50% of thioketone **2** had reacted. After evaporation of the solvent, column chromatography of the residue (silica; benzene–*n*-pentane, 1:3) gave 0.20 g (1 mmol) of unreacted **2** and 0.34 g (0.86 mmol, 86%) of **3-methyl-6,6-diphenyl-2-(mesitylimino)-1-thiacyclohex-3-ene (6d):** mp 126–128 °C (from methanol); IR(CCl_4) 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.01 (br s, 9 H, CH_3), 2.23 (s, 3 H, CH_3), 3.35 (dd, 2 H, CH_2, J = 5.2, 1.8 Hz), 6.30 (m, 1 H, =CH, J = 5.2 Hz), 6.83 (s, 2 H, arom), 7.24 (m, 10 H, arom); ^{13}C NMR ($CDCl_3$) δ 17.60 (q, CH_3), 19.82 (q, 2 CH_3), 20.78 (q, CH_3), 38.31 (t, CH_2), 58.51 (s, CPh_2), 132.59, 134.42, 144.68, 159.43 (s, arom), 188.74 (s, C=N); mass spectrum, m/e 397 (M^+).

Anal. Calcd for $C_{27}H_{27}NS$: C, 81.57; H, 6.85; N, 3.52. Found: C, 81.60; H, 6.81; N, 3.52.

Registry No. **1a**, 82638-89-9; **1b**, 42463-98-9; **1c**, 75340-96-4; **1d**, 82638-90-2; **2**, 1450-31-3; **3a**, 82638-91-3; **3b**, 82638-92-4; **3c**, 82638-93-5; **5**, 82638-94-6; **6c**, 82638-95-7; **6d**, 82638-96-8.

New Synthesis of 1,3-Dithiole and 1,3-Thiazole-2-thiones Promoted by Iron Complexes

Mathias Ngounda, Hubert Le Bozec, and Pierre Dixneuf*

Laboratoire de Chimie de Coordination Organique, Université de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

Received January 18, 1982

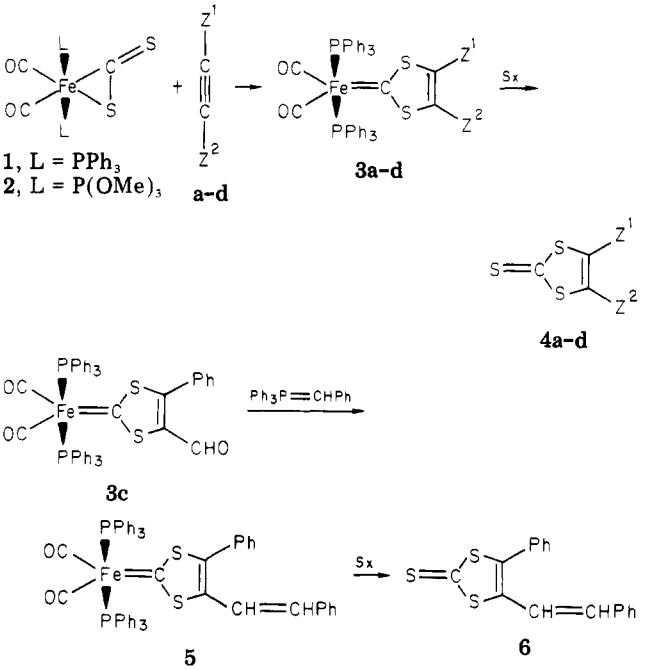
The discovery of electrical conductance properties of charge-transfer complexes which contain tetrathiafulvalene (TTF) as an electron-donating component[1] has initiated an increasing interest for the development of new syntheses of tetrathiafulvalenes and of their precursors.[2] The methods of formation of TTF derivatives depend markedly on the nature of their substituents. TTF itself is conveniently prepared by coupling of an 1,3-dithiolium salt using a tertiary amine,[3] and substituted TTF can be obtained from the phosphoranes resulting either from the addition of an alkyne to the R_3PCS_2 zwitterion or from the deprotonation of the adduct of a phosphine to an 1,3-dithiolium salt.[4,5] Another efficient method is based on the desulfurization reactions of 1,3-dithiole-2-thiones involving either phosphorus(III) derivatives[2,6,7] or transition-metal complexes.[8] 1,3-Dithiole-2-thiones can also be used as precursors of 1,3-dithiolium salts.[2,3]

1,3-Dithiole-2-thiones can be prepared by treatment of ethylene trithiocarbonate with alkynes,[9] but this synthesis is limited to electrophilic alkynes. Recently Benitez and Grunwell[10] reported a convenient route, although it was performed under rather drastic conditions (reactor at 140 °C for 24 h) by reacting an excess of substituted acetylenes with bisamine disulfides and carbon disulfide.

We present here a new route to a variety of 1,3-dithiole-2-thiones and 1,3-thiazole-2-thiones containing functional groups in one step from the easily accessible carbon disulfide–iron and isothiocyanate–iron complexes, respectively.

We have shown recently that a variety of alkynes add readily, at room temperature, to the activated carbon disulfide ligand of $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ complexes **1** (L = PPh_3) and **2** (L = $P(OMe)_3$)[11] to afford the thermally stable

Scheme I[a]



[a] a, $Z^1 = Z^2 = CO_2Me$; b, $Z^1 = Z^2 = CO_2Et$; c, Z^1 = Ph, Z^2 = CHO; d, Z^1 = Ph, $Z^2 = COCH_3$.

(1) (a) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. G. *Solid State Commun.* **1973**, *12*, 1125. (b) Ferraris, J. P.; Cowan, D. O.; Walatka, V.; Perlstein, J. H. *J. Am. Chem. Soc.* **1979**, *95*, 948.

(2) Narita, M.; Pittman, C. H., Jr. *Synthesis* **1976**, 489 and references therein.

(3) Melby, L. R.; Hartzler, H. D.; Sheppard, W. A. *J. Org. Chem.* **1974**, *39*, 2456.

(4) Gonnella, N. C.; Cava, M. P. *J. Org. Chem.* **1978**, *43*, 369.

(5) Sato, M.; Gonnella, N. C.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 930.

(6) Hartzler, H. D. *J. Am. Chem. Soc.* **1973**, *95*, 4379.

(7) Miles, M. G.; Wager, J. S.; Wilson, J. D. *J. Org. Chem.* **1975**, *40*, 2577.

(8) Le Coustumer, G.; Mollier, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 38.

(9) O'Connor, B. R.; Jones, F. N. *J. Org. Chem.* **1970**, *35*, 2002.

(10) Benitez, F. M.; Grunwell, J. R. *J. Org. Chem.* **1978**, *43*, 2917.

0022-3263/82/1947-4000$01.25/0