mixture was left to stand at this temperature for 10 h. The product **3** formed was washed with methylene chloride and dried in vacuo to give **3** (18.5 g, 90%) as an oil; ^{1}H NMR (CD_3CN) δ 1.50 (6 H, t, CH_3), 4.30 (4 H, q, J = 6.5 Hz, CH_2).

Synthesis of (Diethylamino)isobutylmethylsulfonium Tetrafluoroborate (2a). To a solution of 1.55 g (0.0075 mol) of **3** in 3.75 mL of acetonitrile (2 M solution) at -25 °C was added 0.8 g (0.0075 mol) of sulfoxide (+)-(*S*)-**1a**: $[\alpha]_D$ + 64.14° (46.5% e,e); IR (thin film) 1050, 1070 cm^{-1} (S=O); ^{1}H NMR ($CDCl_3$) δ 1.20 (6 H, d, J = 6 Hz, $(CH_3)_2CH$), 2.30 (1 H, m, $(CH_3)_2CH$), 2.65 (3 H, s, CH_3SO), 2.80 (2H, d,, J = 6 Hz, $CHCH_2$). The reaction mixture was stirred for 1 h and warmed slowly to room temperature and then stirred for an additional 1 h at room temperature. Evaporation of the solvent afforded the crude product which was dissolved in methylene chloride (25 mL). After filtration the solvent was evaporated to give the salt **2a** as a slightly yellow liquid. It was washed with ether and dried in vacuo to afford 1.1 g (94%) of **2a**: $[\alpha]_D$ +32.5°; IR (thin film) 950-1180 cm^{-1} (SN); ^{1}H NMR (CD_3CN) δ 1.23 (6 H, d, J = 6 Hz, $(CH_3)_2CH$), 1.50 (6 H, t, J = 7 Hz, $(CH_3CH_2)_2N$), 2.31 (1 H, m, $(CH_3)_2CH$), 3.35 (3 H, s, CH_3S), 3.50 (4H, q, $(CH_3CH_2)_2N$), 4.55 (2 H, m, C HCH_2); n^{23}_D = 1.4110.

According to the procedure described above other aminosulfonium tetrafluoroborates **2** were prepared. Their optical rotations are given in Table I. The IR and ^{1}H NMR data of **2** are given below.

2b: n^{23}_D 1.4140; IR (thin film) 960-1180 cm^{-1} (SN); ^{1}H NMR (CD_3CN) δ 1.00 (3 H, t, J = 6 Hz, $CH_3CH_2CH_2CH_2$), 1.30 (6 H, t, J = 6 Hz, $(CH_3CH_2)_2N$), 1.35-2.05 (4 H, m, $CH_3CH_2CH_2CH_2$), 2.60 (3 H, s, CH_3S), 2.70 (2 H, m, $CH_3CH_2CH_2CH_2$), 3.65 (4 H, q, J = 6 Hz, $(CH_3CH_2)_2N$).

2c: n^{25}_D 1.4355; IR (thin film) 950-1160 cm^{-1} (SN); ^{1}H NMR (CD_3CN) δ 1.35 (6 H, t, J = 6 Hz, $(CH_3CH_2)_2N$), 2.20 (3 H, s, $CH_3C_6H_4$), 2.65 (3 H, s, CH_3S), 4.00 (4 H, q, J = 6 Hz, $(CH_3CH_2)_2N$), (SN); 7.85-8.20 (4 H, m, aromatic).

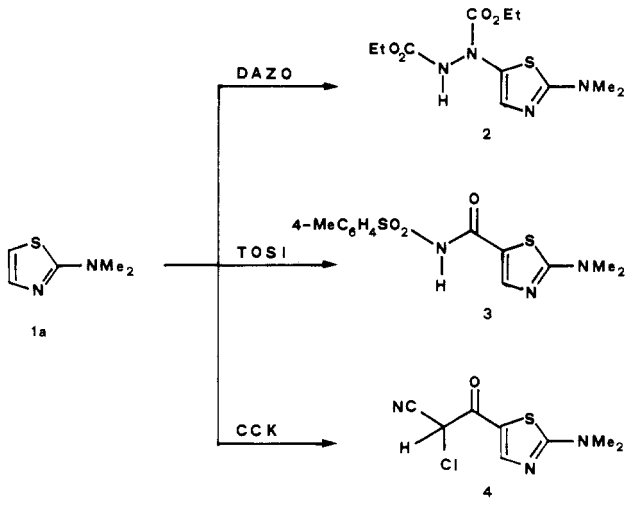
2d: n^{23}_D 1.4850; IR (thin film) 980-1130 cm^{-1} (SN); ^{1}H NMR (CD_3CN) δ 1.30 (6 H, t, J = 6 Hz, $(CH_3CH_2)_2H$), 2.25 (3 H, s, $CH_3C_6H_4$), 3.70 (4 H, q, J = 6 Hz, $(CH_3CH_2)_2N$), 7.90-8.25 (9 H, m, aromatic).

Hydrolysis of 2a. The salt **2a** prepared as above was hydrolyzed with a 0.02 N solution of sodium hydroxide. The aqueous phase was extracted with ether (3 × 20 mL) and chloroform (2 × 20 mL). The combined organic phases were dried over $MgSO_4$. Evaporation yielded 0.72 g (97%) of sulfoxide (-)-(*R*)-**1a**, $[\alpha]_D$ -53.5° (38.8% ee), which had spectral properties indentical with those of the starting sulfoxide (+)-(*S*)-**1a**.

The other salts **2** were hydrolyzed to the corresponding sulfoxides **1** in a similar manner. The optical rotation values and yields of sulfoxides **1** are given in Table I.

Registry No. (*S*)-**1a**, 26451-17-2; (*R*)-**1a**, 62561-56-2; (*R*)-**1b**, 51795-48-3; (*S*)-**1b**, 763-95-1; (*R*)-**1c**, 1519-39-7; (*S*)-**1c**, 5056-07-5; (*R*)-**1d**, 16491-20-6; (±)-**1d**, 77096-69-6; (*S*)-**2a**, 77044-40-7; (*R*)-**2b**, 77060-42-5; (*R*)-**2c**, 77044-42-9; (±)-**2d**, 77044-44-1; **3**, 77044-46-3; ethylsulfinylamine, 77044-47-4; triethyloxonium tetrafluoroborate, 368-39-8.

Scheme I



DAZO = $EtO_2C-N=N-CO_2Et$; TOSI = $4\text{-}MeC_6H_4SO_2-NCO$; CCK = $Cl(CN)C=C=O$

Functionalization of Thiazoles. Selectivity in the Reactions of 2-(Dimethylamino)-1,3-thiazoles with Electrophiles: Formation of Michael-Type Adducts and Thiazolium Salts

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The functionalization of the thiazole ring[1] is generally a difficult task since, owing to the electron-deficient aromatic character, this heterocycle is very resistant to both electrophilic substitutions and additions[2] as well as cycloadditions across the formal C=C and C=N double bonds.[3] We have described recently two new reactions of thiazoles where proper activation of the reactants overcomes this inertness. One is the reaction of 2-bromothiazole with acetylenic esters activated by aluminum trichloride[4] to give *N*-vinylthiazolines, and the other is the reaction of 2-(dimethylamino)thiazoles with *tert*-butylcyanoketene (TBCK)[5] to give pairs of diastereomeric 2:1 cycloadducts (δ-lactones condensed with the thiazole ring across the C_4-C_5 bond) and an open-chain substitution product (Michael-type adduct at C_5 of the thiazole ring).

In view of the activating and directing effect of the dimethylamino group in position 2 of the thiazole ring toward the strong electron acceptor TBCK,[5] we have now investigated the reactions of 2-(dimethylamino)-1,3-thiazoles (**1**) with compounds containing an electron-poor double or triple bond whose reactivity with electron-rich systems is well documented.[6] The aim of this research was to explore the possibility of obtaining [2 + 2] cycloadducts across the C=C double bond[5] of the thiazole ring whose subsequent opening would provide a cis-stereospecific functionalization at this bond and/or achieve a regiospecific substitution at one center of the heterocyclic system. While efforts directed toward the first objective

(1) For recent reviews on thiazoles, see: (a) Iddon, B.; Lowe, P. A. *Org. Compd. Sulphur, Selenium, Tellurium*, **1979**, *5*. (b) Metzger, J. V., Ed., "Thiazole and Its Derivatives"; Wiley: New York, 1979.

(2) See ref 1b, p 99.

(3) Reinhoudt, D. N. *Adv. Heterocycl. Chem.* **1977**, *21*, 253.

(4) Medici, A.; Pedrini, P.; Fogagnolo, M.; Dondoni, A. *J. Chem. Soc., Chem. Commun.*, **1980**, 1077.

(5) Dondoni, A.; Medici, A.; Venturoli, C.; Forlani, L.; Bertolasi, V. *J. Org. Chem.* **1980**, *45*, 621.

(6) In all cases, the actual choice of reactant was based mainly upon stability toward the basicity of thiazoles **1** (see ref 5 and 12). This prevented the use of unhindered activated ethylenes such as 1,1-dicyanoethylene as well as of highly reactive ketenes such as dichloro- and chloroazidoketene, because of their rapid polymerization in the presence of thiazoles **1**. Nevertheless, in addition to those described in the paper, the compounds which have been tested include various electron-poor olephins (acrylonitrile, diethyl maleoate, fumaronitrile, cinnamoyl azide, maleic anhydride, (phenylsulfonyl)ethylene, 2,4-dihydrothiophene 1,1-dioxide, vinyl isocyanate, tetracyanoquinodimethane), acetylenes (dimethyl acetylenedicarboxylate), and azo esters (4-phenyl-1,2,4-triazoline-3,5-dione). Reactivity was explored in apolar (benzene, ethyl ether, CCl_4) and polar (MeCN, CH_2Cl_2, DMF) solvents at room temperature and/or under reflux of the solvent.

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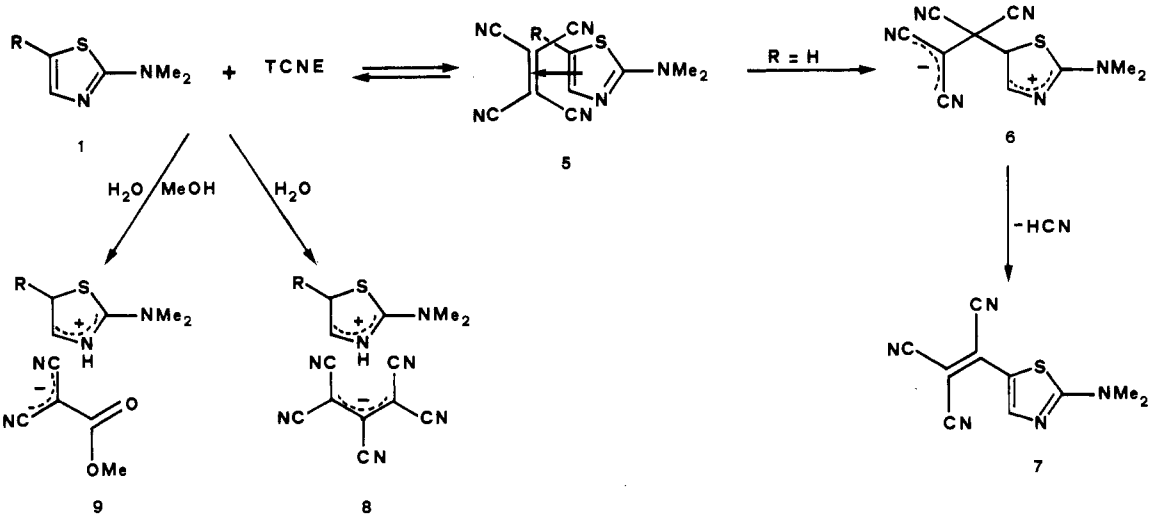
Scheme II[a]



[a] a, R = H; b, R = Me.

have been unsuccessful, we report the formation of open-chain products (Michael-type adducts) as well as thiazolium salts in some cases.

Reactions of 2-(dimethylamino)-1,3-thiazole (**1a**) with diethyl azodicarboxylate (DAZO), tosyl isocyanate (TOSI), and chlorocyanoketene (CCK) in various solvents at room temperature gave the corresponding 1:1 Michael-type adducts **2–4** in high yields (Scheme I). The rates of formation of these adducts were highly solvent dependent and fast in polar media. For instance, the reaction between DAZO and **1a** to give **2** in acetonitrile at room temperature was completed after 24 h, whereas in diethyl ether 14 days was required. Similarly to the pathway suggested for the reaction of **1a** with TBCK,[5] the reactions of Scheme I presumably proceed by electrophilic attack of the nitrogen of DAZO or the cumulene central carbon of TOSI and CCK on the electron-rich C_5 of **1a** to give open-chain dipolar intermediates[7] whose aromatization by loss of the C_5 hydrogen leads to the observed products. The excellent yields of adducts **2–4** and the absence of other adducts (TLC) in the reaction mixtures indicate the high selectivity of these reactions in favor of the Michael-type addition. Other possible reaction products such as bicyclic condensed systems derived from [2 + 2] cycloadditions were not observed, nor was their formation made accessible by the absence of the C_5 hydrogen. In fact, the 5-methylthiazole **1b** was found to be unreactive toward the above and other electrophiles[6] even under more drastic conditions.

An identical selectivity was followed in reactions of tetracyanoethylene (TCNE) with **1a** (Scheme II) in polar solvents such as dichloromethane and acetonitrile to give after 2 h at room temperature the 5-(tricyanovinyl)thiazole **7** in almost quantitative yield (95%). In ethyl ether[8] the reaction was much slower (2 days), and **7** was obtained in lower yield (ca. 50%) together with the thiazolium salt **8a** (ca. 25%). In all solvents, a blue color formed instantly on mixing of the reactants and faded rapidly in acetonitrile and dichloromethane but persisted for several minutes in ethyl ether. Tricyanovinylation by TCNE of aromatic compounds activated by electron-donating substitutents is a quite common reaction[9] for which evidence has been shown to proceed via π and σ complexes. The above observation indicates that a mechanism involving similar types of intermediates can apply also to the tricyanovinylation of **1a**. This presumably consists of the initial formation of the charge-transfer complex **5a** (π complex) which evolves to the dipolar intermediate **6a** (σ complex) by regioselective bond formation between the ethylenic carbon of TCNE and C_5 of the thiazole ring. Reactions carried out in methanol with the aim of trapping the zwitterion **6a** as a solvent adduct[10] resulted only in the reduction of the yield of **7** (ca. 50%) probably because of the consumption of TCNE by methanolysis.[9b]

In a nonpolar solvent such as diethyl ether, the rate of conversion of π complex **5a** into σ complex **6a** is probably slower, and other reactions become competitive with the formation of **7**. The one observed was that leading to 2-(dimethylamino)-1,3-thiazolium pentacyanopropenide (**8a**) arising from decomposition of TCNE by water present in the solvent[8] under the basic catalysis of thiazole **1a**. On the other hand, in the polar solvents acetonitrile and dichloromethane the conversion **5a** → **6a** is presumably very rapid, and the formation of **8a** was negligible. However, when a substituent at C_5 of the thiazole ring inhibited the formation of the σ complex **6**, the thiazolium salt was the sole product of the reaction in both polar and nonpolar media. Thus, 2-(dimethylamino)-5-methyl-1,3-thiazole (**1b**) and TCNE in acetonitrile or ethyl ether[8] gave exclusively the corresponding pentacyanopropenide salt **8b** with no indication of the formation of other products (TLC). From the reaction of **1b** and TCNE in methanol, the only product isolated in low yield (ca. 30%) was the thiazolium methyl dicyanoacetate **9b** whose anion can be formulated to arise from reaction of TCNE with methanol.[9b]

The formation and structure of thiazolium pentacyanopropenides **8a** and **8b** deserve some comments. While these salts are the first examples in the thiazole series, they belong to a well-known class of ammonium

(7) For exemplification of the structure of these intermediates, see compound **6a** in Scheme II and ref 5.

(8) Almost identical results were obtained from reactions in wet commercial solvents without purification and in distilled solvents over proper drying agents (Na wires for ethyl ether and benzene, P_2O_5–$CaCl_2$–molecular sieves for MeCN and CH_2Cl_2). This indicates that the amount of water left in the solvent after purification and/or the amount absorbed on handling the reaction mixture was high enough to give basic hydrolysis of TCNE to pentacyanoallyl anion.[11]

(9) (a) Isaacs, N. S. *J. Chem. Soc.* B **1966**, 1053. Farrell, P. G.; Newton, J.; White, R. F. *Ibid.* **1967**, 637. (b) Ohashi, M.; Suwa, S.; Osawa, Y.; Tsujimoto, K. *J. Chem. Soc., Perkin Trans. 1* **1979**, 2219.

(10) Addition of methanol to **6a** would give a 4-methoxythiazoline derivative. We have already pointed out[5] that the facile 1,2-elimination of methanol from the C_4–C_5 bond of the thiazoline ring makes trapping experiments of these intermediates by this procedure useless.

salts of the cyano carbon acid 1,1,2,3,3-pentacyanopropene which derives from basic hydrolysis of TCNE.[11] The structure of salts 8 stemmed from spectroscopic evidence and the X-ray analysis[12] of compound **8b**. This, inter alia, proves unequivocally that the preferential site for protonation of 2-(dimethylamino)thiazoles 1 is at the endocyclic rather than exocyclic nitrogen in agreement with that suggested from pK_a values[13] and MO calculations.[5] The ^1H NMR spectra of salts 8, in addition to the broad resonance of ^+NH, exhibited identical sets of signals for the corresponding 1,3-thiazoles 1, but shifted dowfield by ca. 0.5 ppm. A downfield shift of the same magnitude has been observed in the spectra of 2-(dimethylamino)-*N*-methylthiazolium iodides.[14] The C resonances in the ^{13}C NMR spectra of 8 were assigned on the basis of off-resonances decoupled spectra and comparison of chemical shift values with those of *N*-methylthiazolium iodides.[14] Also, the salt **9b** was characterized on the basis of its NMR spectra. It is worth noting that while both ^{13}C NMR spectra of 8 showed three signals corresponding to the number of enantiotopic CN groups which can be readily identified in the planar charge-delocalized pentacyanoallyl anion,[12] the spectrum of **9b** exhibited a single signal for the two CN groups, which indicates their equivalence and suggests the preferential dicyanoacetate structure for the anion of this salt. Treatment of the solutions of salts 8 and **9b** in acetone with a slight excess of triethylamine resulted in the immediate formation of the corresponding unprotonated thiazoles 1.

In conclusion, the functionalization at C_5 of the thiazole ring of **1a** has been achieved in a limited number of cases. The reactions provide high regioselectivity and may be employed for the formation of carbon–nitrogen and carbon–carbon bonds in the construction of more complex structures containing the thiazole ring. On the other hand, while the synthetic value of thiazolium salts 8 and 9 is less apparent, these compounds may be of interest to those engaged in the determination of the activity coefficients of ions[15] and in the construction of scales of activity, including that of the proton.[16]

Experimental Section

General Procedures. All melting points are uncorrected. ^1H and ^{13}C NMR spectra were obtained on a 80-MHz Bruker WP 80 spectrometer. Chemical shifts are given in parts per million from Me_4Si. Mass spectra were recorded at 70 eV on a Varian Mat 112 high-resolution spectrometer. IR spectra were obtained (KBr pellets) on a Perkin-Elmer Model 297 grating spectrometer.

2-(Dimethylamino)-1,3-thiazole [**1a**; bp 83–85 °C (15 mmHg)] and 2-(dimethylamino)-5-methyl-1,3-thiazole [**1b**; bp 86–88 °C (15 mmHg)] were prepared as described.[5] For **1a**: ^1H NMR ($(CD_3)_2CO$) δ 3.05 (s, 6, NMe_2), 6.6 (d, 1, =CH(5)), 7.1 (d, 1, =CH(4)); ^{13}C NMR δ 40.3 (q, NMe_2), 107.3 (d, =CH), 140.7 (d, =CH), 172.2 (s, $=CNMe_2$). For **1b**: ^1H NMR δ 2.21 (d, 3, Me), 2.95 (s, 6, NMe_2), 6.7 (q, 1, =CH(4)), ^{13}C NMR δ 11.9 (q, Me), 40.1 (q, NMe_2), 121.3 (s, =C(5)), 137.7 (d, =CH), 170.7 (s, $=CNMe_2$). Tetracyanoethylene (TCNE), diethyl azodicarboxylate (DAZO) and *p*-toluenesulfonyl isocyanate (TOSI) were commercially available. Chlorocyanoketene (CCK) was prepared in situ by thermolysis of the proper azido-2(5*H*)-furanone.[17] All experiments were carried out at room temperature under an N_2 atmosphere in commercial solvents without purification when not otherwise stated.

Reaction of 2-(Dimethylamino)-1,3-thiazole (1a) with Diethyl Azodicarboxylate (DAZO). A solution of 174 mg (1 mmol) of DAZO in 5 mL of acetonitrile was added with stirring to an equivalent solution of thiazole **1a**. After 24 h the solvent was removed under vacuum and the residue was chromatographed (silica, 1:1 benzene–ethyl acetate) to give 270 mg (89%) of 2-(dimethylamino)-5-(1,2-dicarbethoxyhydrazino)-1,3-thiazole (**2**): mp 124–125 °C (from CCl_4); IR (KBr) 3190 (NH), 1740 (C=O), 1715 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (t, 6, 2 CH_3), 3.1 (s, 6, NMe_2), 4.25 (q, 4, 2 CH_2), 7.1 (s, 1, =CH), 7.4 (br, 1, NH); mass spectrum, *m/e* 302 (M^+), 257, 229, 214, 183, 169, 157, 142, 127, 88.

Anal. Calcd for $C_{11}H_{18}N_4O_4S$: C, 43.70; H, 6.0; N, 18.53; S, 10.60. Found: C, 43.52; H, 5.78; N, 18.43; S, 10.45.

A reaction carried out in ethyl ether with the same concentrations of the reactants gave adduct **2** in 92% yield after 14 days.

Reaction of 2-(Dimethylamino)-1,3-thiazole (1a) with *p*-Toluensulfonyl Isocyanate (TOSI). A solution of 250 mg (1.26 mmol) of TOSI in 20 mL of benzene (distilled over Na wires) was added dropwise with stirring to an equivalent solution of thiazole **1a** in 20 mL of the same solvent. A white precipitate formed instantly on mixing the reactants. After the mixture was stirred for 2 h, the precipitate was filtered to give 370 mg (90%) of 2-(dimethylamino)-5-[[(*p*-toluenesulfonyl)amino]carbonyl]-1,3-thiazole (**3**): mp 242–244 °C (from ethanol); IR (KBr) 3245 (NH), 1665 (C=O) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 2.44 (s, 3, CH_3), 2.8 (br, 1, NH), 3.16 (s, 6, NMe_2), 7.4 (d, 2, aromatic), 7.94 (d, 2, aromatic), 8.04 (s, 1, =CH); mass spectrum, *m/e* 325 (M^+), 216, 155, 127, 91.

Anal. Calcd for $C_{13}H_{15}N_3S_2O_3$: C, 47.98; H, 4.65; N, 12.91; S, 19.71. Found: C, 48.13; H, 4.63; N, 12.91; S, 19.48.

Reaction of 2-(Dimethylamino)-1,3-thiazole (1a) with Chlorocyanoketene (CCK). A solution of 400 mg (3.12 mmol) of thiazole (**1a**) in 50 mL of dry benzene (distilled over Na wires) was added under N_2 pressure to a refluxing solution of 588 mg (3.12 mmol) of 4-azido-3-chloro-5-methoxy-2(5*H*)-furanone[17] in 100 mL of dry benzene. After 12 h at room temperature, the solvent was removed under vacuum, and the residue was chromatographed (silica, 95:5 dichloromethane–ethyl acetate) to give 250 mg (35%) of 2-(dimethylamino)-5-(chlorocyanoacetyl)-1,3-thiazole (**4**): mp 125–127 °C (from dichloromethane–*n*-hexane); IR (KBr) 1645 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.25 (s, 6, NMe_2), 5.40 (s, 1, CH), 8.12 (s, 1, =CH); mass spectrum, *m/e* 229 (M^+), 155, 127.

Anal. Calcd for $C_8H_8ClN_3OS$: C, 41.83; H, 3.51; N, 18.29; S, 13.96. Found: C, 41.95; H, 3.45; N, 18.44; S, 13.88.

Reaction of 2-(Dimethylamino)-1,3-thiazole (1a) with Tetracyanoethylene (TCNE). (a) In Dichloromethane or Acetonitrile. A solution of 100 mg (0.78 mmol) of TCNE in 30 mL of solvent was added dropwise with stirring to an equivalent solution of thiazole **1a** in 10 mL of the same solvent. The color of the solution changed gradually from an initial slight blue to green and then to red-brown. After 2 h the solvent was removed under vacuum, and the residue was chromatographed (silica, 1:1 benzene–ethyl acetate) to give 170 mg (95%) of 2-(dimethylamino)-5-(tricyanovinyl)-1,3-thiazole (**7**): mp 207–208 °C (from methanol); IR (KBr) 2220 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.4 (s, 6, NMe_2), 8.20 (s, 1, =CH); mass spectrum, *m/e* 229 (M^+), 214, 200, 187, 160, 139, 105.

Anal. Calcd for $C_{10}H_7N_5S$: C, 52.39; H, 3.08; N, 30.55; S, 13.99. Found: C, 51.97; H, 2.89; N, 30.73; S, 13.58.

(b) In Methanol. A solution of 100 mg (0.78 mmol) of TCNE in 15 mL of methanol was added with stirring to an equivalent solution of thiazole **1a** in 15 mL of the same solvent. After 6 h at room temperature, workup of the reaction mixture as detailed

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(12) Gilli, G.; Bertolasi, V., private communication.
(13) Forlani, L.; Breviglieri, G.; De Maria, P. *J. Chem. Soc., Perkin Trans. 2* **1979**, 163.
(14) Prepared from the corresponding thiazoles **1a** and **1b** and 1 equiv of methyl iodide (nitrobenzene, room temperature, ca. 6 days). 2-(Dimethylamino)-*N*-methylthiazolium iodide: mp 200–205 °C (from petroleum ether); ^1H NMR [$(CD_3)_2CO$ + 1% $(CD_3)_2SO$] δ 3.46, (s, 6, NMe_2), 4.06 (s, 3, ^+NMe), 7.35 (d, 1, =CH), 7.65 (d, 1, =CH); ^{13}C NMR [$(CD_3)_2CO$] δ 43.47 (q), 45.02 (q), 110.58 (d), 136.06 (d), 172.7 (s). 2-(Dimethylamino)-5-methyl-*N*-methylthiazolium iodide: mp 58–60 °C (from petroleum ether); ^1H NMR [$(CD_3)_2CO$] δ 2.38 (d, 3, Me), 3.5 (s, 6, NMe_2), 4.1 (s, 3, ^+NMe), 7.54 (q, 1, =CH); ^{13}C NMR [$(CD_3)_2CO$] δ 12.23 (q), 40.5 (q), 45.1 (q), 121.9 (s), 132.2 (d), 171.7 (s).
(15) Yates, K.; McClelland, R. A. *Prog. Phys. Org. Chem.* **1974**, *11*, 323.
(16) Modro, T. A.; Yates, K.; Janata, J. *J. Am. Chem. Soc.* **1975**, *97*, 1492. Yates, K.; Modro, T. A. *Acc. Chem. Res.* **1978**, *11*, 190.
(17) Moore, H. W. *Acc. Chem. Res.* **1979**, *12*, 125.

above gave 80 mg (50%) of the (tricyanovinyl)thiazole **7** and 80 mg of unreacted thiazole **1a**.

(c) In Diethyl Ether. A solution of 500 mg (3.9 mmol) of TCNE in 600 mL of ethyl ether was added with stirring to an equivalent solution of thiazole **1a** in 20 mL of the same solvent. The color of the solution was initially deep blue, then turned to green, and finally, after 24 h, became red-brown; meanwhile, a gray precipitate was formed. After an additional 24 h, the precipitate was filtered, and we obtained 300 mg (26%) of 2-(dimethylamino)-1,3-thiazolium 1,1,2,3,3-pentacyanopropenide (**8a**): mp 105–107 °C (from dichloromethane–ethyl ether); IR (KBr) 2200 and 2190 (C≡N) cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 3.46 (s, 6, NMe_2), 7.13 (d, 1, =CH), 7.5 (d, 1, =CH), 7.8 (br, 1, NH); ^{13}C NMR [$(CD_3)_2CO$] δ 42.6 (q, NMe_2), 56.7 (s, =C), 109.5 (d, =CH), 115.8 (s, C≡N), 116.8 (s, C≡N), 118.6 (s, C≡N), 128,2 (d, =CH), 159.8 (s, C=), 170.9 (s, $=CNMe_2$).

Anal. Calcd for $C_{13}H_9N_7S$: C, 52.87; H, 3.07; N, 33.20; S, 10.85. Found: C, 52.50; H, 2.95; N, 33.42; S, 11.0.

The filtrate was evaporated, and the residue was chromatographed (silica, 7:3 dichloromethane–ethyl acetate) to give 470 mg (53%) of the (tricyanovinyl)thiazole **7** and 100 mg of unreacted **1a**.

Reaction of 2-(Dimethylamino)-5-methyl-1,3-thiazole (1b) with Tetracyanoethylene (TCNE). (a) In Dichloromethane or Acetonitrile. A solution of 270 mg (2.1 mmol) of TCNE in 90 mL of solvent was added with stirring to an equivalent solution of thiazole **1b** in 30 mL of the same solvent. The reaction solution became initially green and then turned to brown. After 2 h half of the solvent was removed under vacuum, and an equal amount of ethyl ether was added. The resulting precipitate was filtered, and we obtained 160 mg (25%) of 2-(dimethylamino)-5-methyl-1,3-thiazolium 1,1,2,3,3-pentacyanopropenide (**8b**): mp 122–124 °C (from dichloromethane–ethyl ether); IR (KBr) 2220 and 2200 (C≡N) cm^{-1}; ^1H NMR [$(CD_3)_2CO$] δ 2.38 (d, 3, Me), 3.41 (s, 6, NMe_2), 7.2 (q, 1, =CH), 9.8 (br, 1, NH); ^{13}C NMR [$(CD_3)_2CO$] δ 12.1 (q, Me), 42.2 (q, NMe_2), 57.9 (s, =C), 114.2 (s, C≡N), 114.8 (s, C≡N), 117.1 (s, C≡N), 123.5 (s, =C), 124.1 (d, =CH), 136 (s, C=), 170.1 (s, $=CNMe_2$).

Anal. Calcd for $C_{14}H_{11}N_7S$: C, 54.35; H, 3.58; N, 31.69; S, 10.36. Found: C, 54.46; H, 3.68; N, 31.23; S, 10.62.

(b) In Diethyl Ether. A solution of 90 mg (0.70 mmol) of TCNE in 150 mL of solvent was added with stirring to an equivalent solution of thiazole **1b** (99.4 mg) in 20 mL of the same solvent. This resulted in immediate formation of a deep blue color which persisted for more than 1 h and then turned to yellow and finally to red-brown. After 4 days, the precipitate which formed was filtered and identified as the thiazolium salt **8b** (100 mg, 46%). Evaporation of the solvent and chromatography of the residue (silica, 1:1 dichloromethane–ethyl ether) gave 35 mg of unreacted thiazole **1b**.

From a reaction where the molar ratio between TCNE and **1b** was 2:1, the yield of **8b** was 75%.

From a reaction carried out with equivalent amounts of reactants (0.70 mmol) in ethyl ether distilled twice over Na wire was obtained the salt **8b** in ca. 30% yield after 10 days.

(c) In Methanol. A solution of 90 mg (0.78 mmol) of TCNE in 20 mL solvent was added with stirring to an equivalent solution of thiazole **1b** (99.4 mg) in 20 mL of the same solvent. After the mixture was allowed to stand for 24 h, the solvent was evaporated under vacuum, and the residue was crystallized from dichloromethane–ethyl ether to give 60 mg (29%) of 2-(dimethylamino)-5-methyl-1,3-thiazolium 2,2-dicyano-1-methoxy-1-oxoethenide (**9b**): mp 105–107 °C; IR (KBr) 2160 and 2190 (C≡N) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (d, 3, Me), 3.36 (s, 6, NMe_2), 3.64 (s, 3, OMe), 7.01 (q, 1, =CH), 8.8 (broad, 1, NM); ^{13}C NMR ($CDCl_3$) δ 12.29 (q, Me), 33.15 (s, $C(CN)_2$), 42.40 (q, NMe_2), 51.28 (q, OMe), 121.37 (s, =C), 122.36 (s, C≡N), 124.25 (d, =CH), 169.08 and 173.48 (2, s, C=O and $=CNMe_2$.

Anal. Calcd for $C_{11}H_{14}N_4O_2S$: C, 49.61; H, 5.30; N, 21.04; S, 12.04. Found: C, 49.70; H, 5.28; N, 21.16; S, 11.94.

The NMR spectrum of the residue of crystallization showed the presence of unreacted thiazole **1b**.

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Registry No. 1a, 6142-08-1; **1b**, 52963-36-7; **2**, 77080-46-7; **3**, 77080-47-8; **4**, 77080-48-9; **7**, 77080-49-0; **8a**, 77097-70-2; **8b**, 77080-50-3; **9b**, 77080-51-4; tetracyanoethylene, 670-54-2; diethyl azodicarboxylate, 1972-28-7; *p*-toluenesulfonyl isocyanate, 4083-64-1; 4-azido-3-chloro-5-methoxy-2(5*H*)-furanone, 60010-88-0; 2-(dimethylamino)-*N*-methylthiazolium iodide, 31766-83-3; 2-(dimethylamino)-5-methyl-*N*-methylthiazolium iodide, 77080-52-5; chlorocyanoketene, 60010-89-1.

Convenient Synthesis of Unsymmetrical Aryl Sulfides

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In view of our interest in the role played by the substituents in the cleavage of the carbon–sulfur bond in aryl sulfides by means of electrophilic agents,[1] we required a variety of unsymmetrical aryl sulfides of general formula **1** (see Scheme I coupled with Table I), which were largely unknown.

Recent work by Fujisawa and co-workers[2] has shown that the iron-catalyzed *neat* sulfuration of a large excess of aromatic compound with arenesulfenyl chlorides (10:1 molar ratio) can provide a facile synthetic route for such compounds; however, under conditions similar to those reported, expensive and somewhat tedious procedures were required to isolate pure compounds.

We now report a simpler and more expeditious method than the previous one for preparing the required new unsymmetrical aryl sulfides in high yield. Equimolar amounts of arenesulfenyl chlorides **2a–d** and the appropriate aromatic compounds **3a–d** were reacted in nitroethane at room temperature, in a nitrogen atmosphere, according to Scheme I. The reactions proceeded smoothly with the release of hydrogen chloride and subsided within 0.5–1 h to afford the corresponding aryl sulfides **4–19** (Table I). In general, reactions occurred in the absence of catalyst (method A), with the exception of the reactions of arenesulfenyl chlorides **2a–d** with mesitylene **3a**, which were carried out in the presence of tin(IV) chloride as a catalyst (method B).

The choice of mild conditions (temperature and reaction time, absence of light, solvent, and nitrogen stream) is crucial to avoid or minimize disproportionation of sulfenyl chlorides and double sulfuration.[2] Furthermore, *isolation of the products is achieved by simply evaporating the solvent, followed by crystallization or distillation.*

On the other hand, owing to decreased strength of (4-nitrophenyl)sulfenyl chloride as electrophilic agent,[2] sulfides **20–23**, bearing a nitro group in the para position, were prepared traditionally by nucleophilic condensation of *p*-nitrochlorobenzene with the appropriate potassium thiolate in refluxing ethanol (method C). The hitherto unreported 2,4,6-trimethoxythiophenol (**26**) and 3-chloro-2,4,6-trimethoxythiophenol (**27**) were prepared in

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(2) T. Fujisawa, T. Kobori, N. Otsuka, and G. Tsuchihashi, *Tetrahedron Lett.*, 5071 (1968).

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