NH_2), 39.7 (CH_2NH_2), 40.5 (CH_3), 56.2 (NCH_2); ^{1}H NMR (D_2O) δ 2.15 (m, 8 H, CH_2CH_2), 3.25 (s, 3 H, CH_3), 3.45 (m, 8 H, CH_2N); mass spectrum, *m/e* (relative intensity) 174 (M^+ + 1, 7). Anal. Calcd for $C_9H_{23}N_3\cdot 3HCl$: C, 38.2; H, 9.2; N, 14.9. Found: C, 38.3; H, 9.3; N, 14.7.

Acknowledgment. This work was made possible by Grant GM-11973 from the NIH (PHS). The help of CONICET (Argentina) is also acknowledged.

Registry No. 1, 31058-09-0; 2, 89690-18-6; 3, 89690-09-5; 4, 89690-17-5; 5, 103-67-3; 6, 14321-27-8; 7, 2032-33-9; 8, 2403-22-7; 9, 89690-05-1; 10, 89690-06-2; 11, 89690-07-3; 12, 89690-08-4; 13, 89690-10-8; 14, 89690-11-9; 15, 89690-12-0; *N*-ethylputrescine diethylcarbamate, 89690-13-1; *N*-propylputrescine diethylcarbamate, 89690-14-2; *N*-butylputrescine diethylcarbamate, 89690-15-3; *N*-methylputrescine diethylcarbamate, 89690-16-4; methylamine, 74-89-5; benzylidenemethylamine, 622-29-7; benzylideneethylamine, 6852-54-6; benzylidenepropylamine, 6852-55-7; benzylidenebutylamine, 1077-18-5; 4-bromobutyronitrile, 5332-06-9.

Oxidative Hydrolysis of γ-Thioacetalated Phosphonium Salts. Influence of the Counterion on the Course of the Reaction

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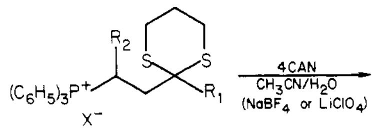
Received October 31, 1983

A fast reaction and an easy workup make cerium(IV) ammonium nitrate (CAN) an attractive reagent for oxidative hydrolysis of 1,3-dithianes to the corresponding carbonyl compounds.[1] We proposed a mechanism based on electron transfer from sulfur to the metal followed by chemical reaction with the medium[2] that is essentially identical with the one proposed for the electrochemical hydrolysis.[3] We have already stated[4] that the electrochemical oxidation can be complicated by the presence of halide counterions, and ion exchange with nonoxidizable counterions is advantageous. We report here on oxidative hydrolysis of γ-thioacetalated phosphonium fluoroborates, perchlorates, or nitrates with cerium(IV) and emphasize the "abnormal" oxidation of nitrate salts.

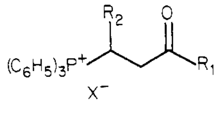
The oxidation of phosphonium fluoroborates **1a–e** or perchlorates **1a′–e′** by 4 equiv of cerium(IV) affords, in good yield, the expected γ-aldehydic or ketonic phosphonium salts **2a–e** and **2a′–e′** (Scheme I).

Scheme I



1

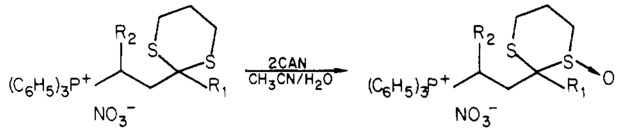
a (X^- = BF_4^-), a′ (X^- = ClO_4^-): R_1 = CH_3; R_2 = H
b (X^- = BF_4^-), b′ (X^- = ClO_4^-): R_1 = CH_3; R_2 = CH_3
c (X^- = BF_4^-), c′ (X^- = ClO_4^-): R_1R_2 = $-(CH_2)_3-$
d (X^- = BF_4^-), d′ (X^- = ClO_4^-): R_1 = H; R_2 = CH_3
e (X^- = BF_4^-), e′ (X^- = ClO_4^-): R_1 = H; R_2 = C_6H_5



2

yield, %	
a, 83	a′, 80
b, 87	b′, 75
c, 58	c′, 67
d, 68	d′, 74
e, 75	e′, 82

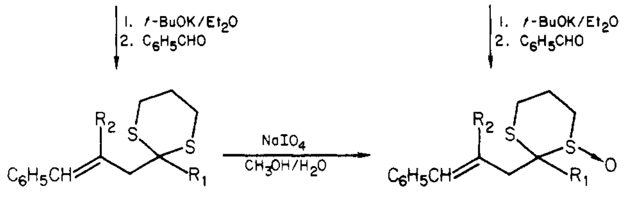
Scheme II



3 **4**

a, R_1 = CH_3; R_2 = H
b, R_1R_2 = $-(CH_2)_3-$
c, R_1 = H; R_2 = H

	IR(ν_{S-O}), cm^{-1}	yield (%)
a	1030	75
b	1030	68
c	1028	63



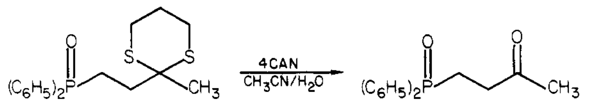
6a (yield = 93%)

5

	IR(ν_{S-O}), cm^{-1}	yield (%)
a	1052, 1041	70 ($NaIO_4$:80)
b	1050, 1032	75
c	1052, 1041	67

The oxidation of γ-thioacetalated ketonic or aldehydic phosphonium nitrates **3a–c** (Scheme II) does not consume 4 equiv of cerium(IV) but is complete after 2 equiv of reagent are added. The ^{1}H NMR spectra of isolated compounds **4** (Scheme II) indicate the presence of the dithiane group, and the IR spectra show a new strong absorption near 1030 cm^{-1} which can be attributed to a sulfoxide group. The elimination of the triphenylphosphonio group by a Wittig reaction with benzaldehyde affords the olefin **5** in which the presence of an oxygen was determined by mass spectrometry and evidence for a sulfoxide group was given by IR (strong absorption near 1030 cm^{-1}). Olefin **5a** also was independently prepared by a Wittig reaction of **3a** with benzaldehyde[5] followed by the oxidation of **6a** with sodium periodate to the corresponding monosulfoxide.[6]

This is, to our knowledge, the first example of oxidation of a 1,3-dithiane to a monosulfoxide by cerium(IV). This "abnormal" oxidation pathway requires the presence of a phosphonium group with a nitrate counterion. Indeed, phosphine oxide **7** with only a partial positive charge on



7 **8** (yield = 79%)

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(1) Gröbel, B. T.; Seebach, D. *Synthesis* **1977**, 357.

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(4) Cristau, H. J.; Chabaud, B.; Niangoran, C. *J. Org. Chem.* **1983**, *48*, 1527.

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(6) Carey, F. A.; Dailey, O. D.; Hernandez, O.; Tucker, J. R. *J. Org. Chem.* **1976**, *41*, 3975.

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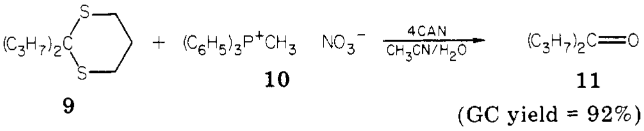
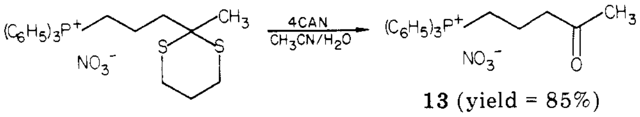
phosphorus follows the "normal" reactivity pattern and is converted into the γ-keto alkyl phosphine oxide **8**. Furthermore, this new reactivity corresponds to a solvent cage ion pair process. Indeed, when an equimolecular mixture of dithiane **9** and phosphonium nitrate **10** is oxidized by 4 equiv of CAN, the corresponding di-*n*-propyl ketone **11** can be prepared in excellent yield. The electrochemical oxidation of phosphonium nitrates **3a–c** in presence of tetraethylammonium nitrate as supporting electrolyte affords also sulfoxides **4a–c**. This is in good agreement with an outer-sphere oxidation by cerium(IV), which does not imply the participation of a nitrate ligand on the metal but the nitrate on the phosphonium.



9 10 11 (GC yield = 92%)

Finally, this interaction between nitrate and dithiane depends on the size of the molecule. The oxidation of δ-thioacetalated phosphonium nitrate **12** with one more carbon in the chain between triphenylphosphonio and dithiane groups result in the exclusive formation of δ-keto phosphonium salt **13** by normal hydrolysis of the 1,3-dithiane group.



12

13 (yield = 85%)

This specific R_3P^+/NO_3^-/dithiane interaction involves likely a double hard–hard interaction between nitrate, phosphorus, and the sulfur radical–cation generated by a one-electron oxidation of the starting material.[2] Analogous interactions have been already encountered in basic hydrolysis of ammonium[7] and phosphonium salts.[8]

In conclusion, the particular reactivity of γ-thioacetalated phosphonium nitrates comes both from chemical and stereochemical requirements, which are the presence of a nitrate counterion and a phosphorus at 2 carbon atoms from the dithiane group.

Experimental Section

Measurements. Melting points are uncorrected and were measured by using an automatic Mettler FP-51 apparatus (heating rate 2 °C/min). Infrared spectra were recorded on a Perkin-Elmer 221 spectrometer by using samples as films or KBr disks. ^1H NMR spectra were measured with a Varian EM-360 L spectrometer with Me_4Si as internal standard. ^{31}P NMR spectra (reference H_3PO_4, 86% in water) were recorded on a Brücker WP 80 DS spectrometer. Microanalyses of new compounds are listed in Table I.

Synthesis of γ-Thioacetalated Phosphonium Fluoroborates 1a–e and Perchlorates 1a′–e′. Phosphonium fluoroborates and perchlorates were prepared from the bromide[9] by the addition of sodium fluoroborate or lithium perchlorate (10 mmol) to a stirred solution of the phosphonium bromide (5 mmol) in acetonitrile (80 mL). After 10 min at room temperature the solvent was removed in vacuo, the residue was diluted with chloroform (100 mL), and the organic phase was washed with water (20 mL, 2 times), dried (Na_2SO_4), concentrated in vacuo to about 20 mL, and added dropwise to ether (200 mL). The precipitate obtained was dried and recrystallized (acetone:ethyl acetate, 20:80). **1a** (hemihydrate): yield 90%; mp 225 °C; ^{31}P NMR δ 25.45. **1b**: yield 95%; mp 161 °C; ^{31}P NMR δ 32.29. **1c**: yield 87%; mp 235 °C; ^{31}P NMR δ 26.82. **1d**: yield 92%; mp182 °C; ^{31}P NMR δ 27.28. **1e**: yield 78%; mp 229 °C; ^{31}P NMR δ 24.49. **1a′**: yield 78%; mp 232 °C; ^{31}P NMR δ 24.22. **1b′**: yield 84%; mp 167 °C; ^{31}P NMR δ 32.29. **1c′**: yield 88%; mp 162 °C; ^{31}P NMR δ 25.86. **1d′**: yield 93%; mp 105 °C; ^{31}P NMR δ 30.04. **1e′**: yield 86%; mp 240 °C; ^{31}P NMR δ 24.90.

Table I. Microanalytical Data for New Compounds

	calcd			found		
cmpd	C	H	N	C	H	N
5a	63.18	6.82		62.95	6.78	
5b	65.71	6.86		65.64	6.93	
5c	61.86	6.93		61.52	6.28	
7	62.96	6.40		62.96	6.30	
8[a]	68.32	6.09		68.59	6.46	
12	62.50	6.05	2.80	62.59	6.19	2.53
13	67.47	5.91	3.42	67.38	5.92	3.44

[a] Hemihydrate.

Cerium(IV) Hydrolysis of γ-Thioacetalated Phosphonium Fluoroborates 1a–e and Perchlorates 1a′–e′. CAN (8 mmol) was added in small portions to a solution of the phosphonium salt (2 mmol) and sodium tetrafluoroborate or lithium perchlorate (10 mmol) in $CH_3CN:H_2O$, 90:10 (50 mL). The reaction was stirred at room temperature until the starting orange color turned to pale-yellow (10–15 min). The reaction mixture was then filtrated and the organic phase concentrated in vacuo. The residue was diluted with chloroform (100 mL), and the organic phase washed with water (20 mL, 2 times), dried (Na_2SO_4), concentrated to about 20 mL, and added dropwise to ether (200 mL). The precipitate was dried and recrystallized (acetone:ethyl acetate, 20:80). Characterization of compounds was done by comparison of melting points and IR spectra of the perchlorate form (after anion exchange for compounds **1a–e** following the procedure previously described) with those of authentic samples.[4]

Cerium(IV) Hydrolysis of γ-Thioacetalated Phosphonium Nitrates 3. Physical properties of salts **3** have been already described.[4] The same procedure used for hydrolysis of salts **1** was followed by using 2 equiv of CAN. The precipitate was carefully dried (P_2O_5, 80 °C, 1–2 torr, 24 h) and used without further purification for the Wittig reaction with benzaldehyde.

Synthesis of Olefins 5 and 6. Carefully dried (vide supra) phosphonium salt **3** or **4** (4 mmol) was added, under nitrogen, to a suspension of potassium *tert*-butylate (4.1 mmol) in anhydrous ether (50 mL), and the reaction mixture was stirred at room temperature for 1 h. Freshly distilled benzaldehyde (6.4 mmol) was added and stirring was continued for 15 h. The reation mixture was filtrated and concentrated in vacuo, the residue was diluted with chloroform (100 mL), and the organic phase was washed with water (20 mL, 2 times), dried (Na_2SO_4), and concentrated in vacuo to an oily residue, which was chromatographed (silica gel, hexane:ethyl acetate, 95:5) to yield the olefin **5** or **6** as sticky oil materials. **5a**: IR (CCl_4) ν_{S-O} 1052, 1041 cm^{-1}; NMR ($CDCl_3$) δ 7.33 (s, 5 H, C_6H_5), 6.68 (dt, 1 H, J = 1.8 Hz, J = 12 Hz), 5.68 (dt, 1 H, J = 7 Hz, J = 12 Hz), 2.97 (dd, 2 H, J = 7 Hz, J = 1.8 Hz), 2.83–2.13 (m, 6 H), 1.63 (s, 3 H, CH_3); MS (70 ev), *m/e* 266 (M^+), 175 ($M^+ - C_7H_7$). **5b**: IR (CCl_4) ν_{S-O} 1050, 1032 cm^{-1}; NMR ($CDCl_3$) δ 7.3 (s, 5 H, C_6H_5), 6.56 (s, 1 H), 3.06–2.73 (m, 4 H), 2.63–1.67 (m, 10 H); MS (70 ev), *m/e* 292 (M^+). **5c**: IR (CCl_4) ν_{S-O} 1052, 1041 cm^{-1}; NMR ($CDCl_3$) δ 7.33 (s, 5 H, C_6H_5), 6.65 (dt, 1 H, J = 1.5 Hz, J = 12 Hz), 5.75 (dt, 1 H, J = 7 Hz, J = 12 Hz), 3.93–1.93 (m, 9 H); MS (70 ev), *m/e* 252 (M^+), 161 ($M^+ - C_7H_7$).

Sodium Periodate Oxidation of Olefin 6. Sodium periodate (3.1 mmol) dissolved in water (8 mL) was added to **6** (2.8 mmol) dissolved in methanol (30 mL). The reaction mixture was stirred for 1 h at room temperature, filtrated and concentrated in vacuo. The residue was diluted with chloroform (100 mL), and the organic layer was washed with water (20 mL, 2 times), dried (Na_2SO_4), and concentrated to yield **5a** as an oily residue which was chromatographed as previously described.

[3,3-(Dithiotrimethylene)butyl]diphenylphosphine Oxide (7). The corresponding γ-thioacetalated phosphonium bromide[8]

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(9) γ-Thioacetalated phosphonium bromides were prepared according to Cristau et al. (Cristau, H. J.; Vors, J. P.; Christol, H. *Synthesis* **1979**, 538).

(12 mmol) in dichloromethane (70 mL) and sodium hydroxide 125 mmol) in water (25 mL) were stirred at reflux for 48 h. The organic phase was washed with water (10 mL, 2 times), dried (Na_2SO_4), concentrated in vacuo, yielding crystalline 7. Recrystallization from hexane/benzene gave pure 7, mp 103 °C, in 85% yield: IR $\nu_{P=O}$ 1190 cm^{-1}; ^{1}H NMR δ 8.05–7.3 (m, 10 H, C_6H_5), 3.03–1.67 (m, 10 H), 1.53 (s, 3 H, CH_3); ^{31}P NMR δ 32.63.

(3-Oxobutyl)diphenylphosphine Oxide (8). Oxidation of 7 (1.4 g, 4.69 mmol) by the same procedure as for 1 gave 8 as an oily residue, which was chromatographed (silica gel, chloroform:methanol, 95:5) to pure 8 as a viscous oil in 79% yield: IR (film) $\nu_{C=O}$ 1712 cm^{-1}, $\nu_{P=O}$ 1180 cm^{-1}; ^{1}H NMR 8.0–7.3 (m, 10 H, C_6H_5), 3.1–2.23 (m, 4 H), 2.13 (s, 3 H, CH_3); ^{31}P NMR δ 32.43.

[4,4-(Dithiotrimethylene)pentyl]triphenylphosphonium Nitrate (12). This compound was prepared from the bromide according to a method already described[4] and recrystallized from chloroform/ethylacetate (10:90): yield 93%; mp 109 °C; ^{1}H NMR δ 8.13–7.57 (m, 15 H, C_6H_5), 4–3.33 (m, 2 H, $(C_6H_5)_3P^+CH_2$), 3.33–1.55 (m, 10 H), 1.43 (s, 3 H, CH_3).

(4-Oxopentyl)triphenylphosphonium Nitrate (13). Oxidation of 12 (1.5 g, 2.9 mmol) by the same procedure as for 1 gave crystalline 13. Recrystallization from chloroform/ethyl acetate (10:90) gave pure 13, mp 185 °C, in 85% yield: IR $\nu_{C=O}$ 1712 cm^{-1}; ^{1}H NMR δ 8.1–7.53 (m, 15 H, C_6H_5), 3.9–3.27 (m, 2 H, $(C_6H_5)_3P^+CH_2$), 3.17–2.77 (m, 2 H), 2.16 (s, 3 H, CH_3), 2.27–1.60 (m, 2 H).

Electrochemical Oxidation of Salts 3a–c. Electrochemical equipment and techniques have been described elsewhere.[4] A solution of salt **3** (2 mmol) and tetraethylammonium nitrate (10 mmol) in $CH_3CN:H_2O$, 90:10 (100 mL), was oxidized at 1.5 V until the current had decayed to 10% of its initial value. The reaction mixture was concentrated and diluted with chloroform (200 mL), and the organic phase washed with water (30 mL, 3 times), dried (Na_2SO_4), concentrated in vacuo to about 20 mL, and added dropwise to ether (200 mL). The precipitate was dried (P_2O_5, 80 °C, 1–2 torr, 24 h) to give **4a**, yield 82%, **4b**, yield 64%, and **4c**, yield 58%.

Registry No. **1a** ($X^- = BF_4^-$), 89637-26-3; **1a** ($X^- = Br^-$), 71864-06-7; **1a′**, 89637-31-0; **1b** ($X^- = BF_4^-$), 89637-27-4; **1b** ($X^- = Br^-$), 71864-07-8; **1b′**, 89637-32-1; **1c** ($X^- = BF_4^-$), 89637-28-5; **1c** ($X^- = Br^-$), 80799-65-1; **1c′**, 89637-33-2; **1d** ($X^- = BF_4^-$), 89637-29-6; **1d** ($X^- = Br^-$), 72641-24-8; **1d′**, 89637-34-3; **1e** ($X^- = BF_4^-$), 89637-30-9; **1e** ($X^- = Br^-$), 72641-25-9; **1e′**, 89637-35-4; **2a**, 43064-87-5; **2a′**, 43101-01-5; **2b**, 89637-36-5; **2b′**, 85067-01-2; **2c**, 89637-37-6; **2c′**, 85067-05-6; **2d**, 89637-38-7; **2d′**, 85067-07-8; **2e**, 89637-39-8; **2e′**, 85067-09-0; **3a**, 85066-89-3; **3b**, 85082-15-1; **3c**, 89637-41-2; **4a**, 89637-43-4; **4b**, 89637-45-6; **4c**, 89637-47-8; **5a**, 89637-48-9; **5b**, 89655-99-2; **5c**, 89637-49-0; **6a**, 72641-41-9; 7, 87177-89-7; 8, 67217-31-6; **9**, 79032-15-8; **10**, 35171-92-7; 11, 123-19-3; **12**, 89637-51-4; **13**, 89637-53-6; CAN, 16774-21-3; sodium fluoroborate, 13755-29-8; lithium perchlorate, 7791-03-9; benzaldehyde, 100-52-7.

Synthesis of Pyrrolyl Sulfides

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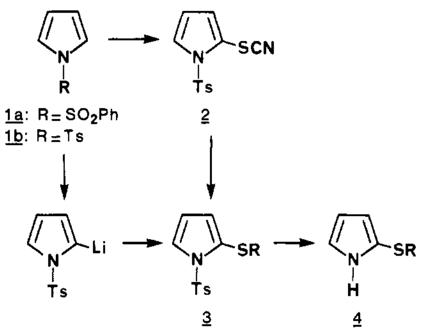
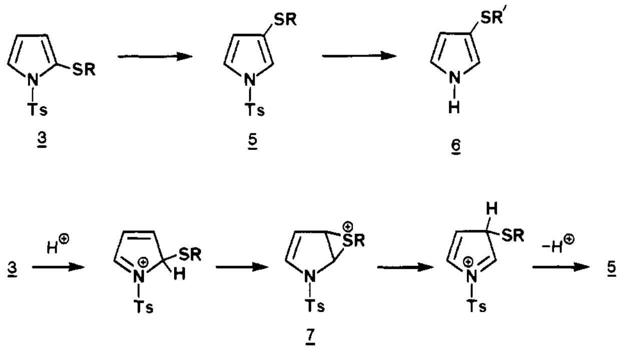
Received November 22, 1983

Recently we[1,2] and others[3] have reported that *N*-(phenylsulfonyl)pyrrole (**1a**)[4] is a valuable substrate in electrophilic subsititution reactions, in particular, for the regioselective introduction of acyl groups at the 3-position. In a continuation of studies on electrophilic substitution of the *N*-(arylsulfonyl)pyrrole nucleus, we have explored the reactions with sulfur electrophiles, with the ultimate objective being to devise a general method for the preparation of rare 3-pyrrolyl sulfides.[5] In contrast to the facile 3-acylations, all attempts to introduce sulfur electrophiles directly at the 3-position of **1** failed (e.g., reaction of **1** with benzenesulfenyl chloride yielded a complex mixture). However, we have found a useful alternative method in which 3-pyrrolyl sulfides may be synthesized from readily available *N*-tosyl-2-pyrrolyl sulfides **3**.

Scheme I



Scheme II



The 2-pyrrolyl sulfides **3** were prepared by the following two procedures (Scheme I): (1) *N*-tosylpyrrole (**1b**)[4] was thiocyanated with ClSCN by using conventional methods[6] to afford a 69% yield of the 2-(thiocyanato)pyrrole **2**,[7] which on treatment with alkyl halides in aqueous NaOH and *tert*-butyl alcohol[8] gave essentially quantitative yields of 2-alkylthioprroles **3**. (2) The 2-phenylthio derivative **3f** was obtained in 70% yield from **1b**, when **1b** was metalated[9,10] with *n*-BuLi in THF for 5 min and subsequently reacted with $PhSSO_2Ph$[11] at −40 °C for 1 h. Alkaline hydrolysis of **3** afforded 1-H-2-pyrrolyl sulfides **4** in excellent yields.

In a key observation, it was found that the 3-thiosubstituted pyrroles **5** are readily available from **3** by isomerization with trifluoroacetic acid (TFA): **3** rearranges cleanly to **5** with a 1:1 mixture of TFA and 1,2-dichloro-

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[7] No product derived from thiocyanation at the 3-position of **1b** could be detected in the crude reaction mixture. When **1b** was reacted with $(SCN)_2$ in dichloromethane in the presence of $AlCl_3$ (2 equiv), 2,5-bis(thiocyano)-*N*-tosylpyrrole, mp 130-132 °C, was obtained along with **2**.

[8] When this reaction was carried out in methanol instead of *tert*-butyl alcohol, the 2-methylthio derivative **3** (R = Me, mp 64–66 °C) was produced as the byproduct. This behavior in the case of other (thiocyano)pyrroles was observed elsewhere: Olsen, R. K.; Snyder, H. R. *J. Org. Chem.* **1965**, *30*, 187.

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