5.14; N, 10.21. Found: C, 61.32; H, 5.10; N, 10.26.

6,6′-Dibromo-2,2′-(ethylenedioxy)dipyridine (16): mp 150–152 °C; 4%; identical with a known sample.

2-[2-(6-Bromopyridyloxy)]ethanol (18): traces (<1%); NMR ($CDCl_3$) δ 3.90 (m, β-CH_2O, 2 H), 4.40 (m, α-CH_2O, 2 H), 6.68 (dd, 3-Pyr-H, J = 8,2 Hz, 1 H), 7.01 (dd, 5-Pyr-H, J = 8, 2 Hz, 1 H), 7.41 (t, 4-Pyr-H, J = 8 Hz, 1 H).

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Registry No.—3, 109-04-6; 4, 61463-64-7; 6, 56446-62-9; 7, 56446-63-0; 8, 56446-64-1; 9, 56446-65-2; 10a, 626-05-1; 10b, 2402-78-0; 11, 56467-84-6; 12, 56446-66-3; 13, 56446-67-4; 14, 56446-68-5; 15, 56446-69-6; 16, 56446-70-9; 17a, 61463-65-8; 17b, 61463-66-9; 18, 61463-67-0; 22, 56446-71-0; 23, 61463-68-1; 26, 61463-69-2; 27, 61463-70-5; 28, 61463-71-6; 29, 56446-73-2; 30, 61463-72-7; 31, 61463-73-8; 32, 61463-74-9; 34, 61463-75-0; 35, 61463-76-1; 37, 61463-77-2; 38, 56446-41-4; bis(2-ethoxymethyl) ether, 112-36-7; 2-ethoxyethanol, 110-80-5; ethylene glycol, 107-21-1; diethylene glycol, 111-46-6; triethylene glycol, 112-27-6; 1-methyl-3,6-dioxa-1,8-octanediol, 61463-78-3; propylene oxide, 75-56-9; tetraethylene glycol, 112-60-7; pentaethylene glycol, 4792-15-8; hexaethylene glycol, 2615-15-8.

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Heterocyclic Amines. 7.[1] Preparation and Reactions of 2- and 3-Thienyl Isothiocyanates

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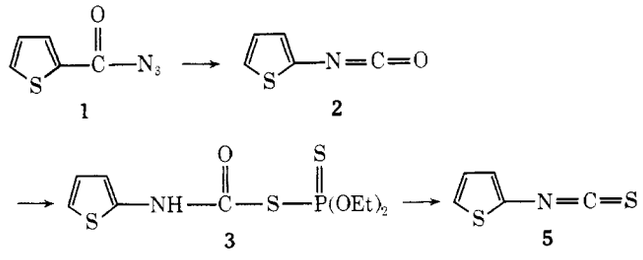
Both 2- and 3-thienyl isothiocyanates have been prepared by thermal rearrangement of the corresponding *S*-(*N*-thienylcarbamoyl)-*O,O′*-diethyl dithiophosphates. These isothiocyanates have been reacted with a variety of amines, alcohols, and mercaptans to synthesize the 2- and 3-thienyl thioureas, thioncarbamates, and dithiocarbamates.

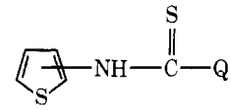
Isothiocyanates of thiophene have not been previously reported. The classical procedures for the synthesis of aromatic-type isothiocyanates[2] require the corresponding primary amines, which are difficultly accessible in the thiophene series, and require conditions which decompose the unstable aminothiophenes.[1,3,4] Thienyl isocyanates are readily available by Curtius rearrangement of thenoyl azides,[5,6] but the "thio-Curtius" rearrangement does not take place. Attempted preparation of thioacyl azides yields the cyclized thiatriazoles, which thermally decompose to nitriles[7] and sulfur, although small amounts of isothiocyanates have been detected by ultraviolet photolysis[8] of thiatriazoles. Ottmann and Hooks[9] prepared isothiocyanates by thermal decomposition of the reaction product obtained from isocyanates and *O,O′*-diethyl hydrogen dithiophosphate. We have found that by modifying their conditions, it is possible to apply this reaction in the thiophene series to prepare both 2- and 3-thienyl isothiocyanates.



Thenoyl azide (1) was thermally rearranged in boiling carbon tetrachloride to thienyl isocyanate (2). This was reacted with *O,O′*-diethyl hydrogen dithiophosphate, and upon cooling, *S*-(*N*-thienylcarbamoyl)-*O,O′*-diethyl dithiophosphate (3) crystallized. This was thermally rearranged to the thienyl isothiocyanate (5).

Because the thienyl isothiocyanates are labile in acid, it was found necessary to minimize their contact with the

Table I. Additional Derivatives of the Thienyl Isothiocyanates



Compd	Thienyl position	Q	% yield	Mp, °C	Recrystn solvent
7	2	$-NH_2$	53	186–186.5	Water
8	3	$-NH_2$	11	192–193	Water
10	3	$-NHPr(n)$	21	54–55	Toluene–ligroin
11	2	$-NHBu(t)$	47	162–162.5	None
12	3	$-NHBu(t)$	47	161–161.5	Toluene
14	3	$-OPr(n)$	57	67.5–68	Ligroin
16	3	$-OBu(t)$	21	109–110 dec	Petroleum ether
17	2	$-SPr(n)$	44	Oil	
18	3	$-SPr(n)$	13	46.5–47	Ligroin

thiophosphoric acid coproducts which codistilled from the reaction mixture. This was accomplished by chromatography after which the thienyl isothiocyanates could be successfully redistilled.

To establish the utility of the thienyl isothiocyanates as intermediates for the synthesis of 2- and 3-thienyl substituted thioureas, thiocarbamates, and dithiocarbamates, suitable conditions were worked out for the reaction of these isothiocyanates with a variety of amines, alcohols, and mercaptans. Compounds in addition to those described in the Experimental Section are listed in Table I.

Experimental Section

All melting points are uncorrected. All NMR spectra were taken on Varian A-60 or T-60 instruments with internal tetramethylsilane reference.

***S*-[*N*-(2-Thienyl)carbamoyl]-*O,O'*-diethyl Dithiophosphate (3).** A solution of 2-thenoyl azide[5] (8.0 g, 52 mmol) in 50 mL of carbon tetrachloride was heated under reflux under anhydrous conditions for 17 h. Half of the solvent was removed by distillation, the residual solution was cooled to room temperature, and while the temperature of the stirred reaction mixture was maintained below 40 °C, 9.20 g (49 mmol) of *O,O'*-diethyl hydrogen dithiophosphate was added dropwise. A few minutes after the addition was complete, stirring was discontinued and the reaction mixture was cooled in the refrigerator. The yield of crude crystalline product was 15.5 g (100%). Part of this material was recrystallized from *n*-heptane, in which the product is of low solubility (ca. 1 g per 400 mL) at the recrystallization temperature of 60 °C. No decomposition was detected when the recrystallization was carried out at 60 °C, but at 70 °C noticeable decomposition occurred. The colored impurities did not dissolve and were removed by filtration. After two recrystallizations the product melted at 103.5–104.5 °C dec, white needles: NMR ($CDCl_3$) δ 1.38 (t, 6, CH_3), 4.27 (octet, 4, CH_2), 6.73–7.00 (m, 3, thienyl H), 9.50 (br band, 1, NH); J_{CH_2,CH_3} = 7.5, J_{POCH_2} = 9.5 Hz.

Anal. Calcd for $C_9H_{14}NO_3PS_3$: C, 34.71; H, 4.53; N, 4.50; P, 9.95; S, 30.89. Found: C, 34.83; H, 4.58; N, 4.54; P, 10.16; S, 30.64.

***S*-[*N*-(3-Thienyl)carbamoyl]-*O,O'*-diethyl dithiophosphate (4)** was prepared similarly to the above, from 24.1 g (0.16 mol) of 3-thenoyl azide[6] and 27.6 g (0.15 mol) of *O,O'*-diethyl hydrogen dithiophosphate. The product was decolorized with acid-washed Norit A charcoal and recrystallized from *n*-heptane: yield 35.0 g (76%); mp 83.5–85.0 °C; NMR ($CDCl_3$) δ 1.39 (t, 6, CH_3), 5.97 (octet, 4, CH_2), 7.03 (q, 1, 4-H), 7.25 (q, 1, 5-H), 7.44 (q, 1, 2-H), 9.07 (br band, 1, NH); $J_{2,4}$ = 1.5, $J_{2,5}$ = 3.2, $J_{4,5}$ = 5.2, J_{CH_2,CH_3} = 7.2, J_{POCH_2} = 10 Hz.

Anal. Calcd for $C_9H_{14}NO_3S_3P$: C, 34.71; H, 4.53, N, 4.50; P, 9.95; S, 30.89. Found: C, 34.80; H, 4.88; N, 4.65; P, 9.93; S, 30.57.

2-Thienyl Isothiocyanate (5). Crude **3** (319 g, 1.03 mol) was pyrolyzed under reduced pressure using an oil bath heated to 150 ± 5 °C. Crude product distilled at 108–114 °C (7 mm). The NMR spectrum indicated that it was less than 50% of the desired product, much of the remainder being various thiophosphates. This material was then chromatographed, in six approximately equal batches, on dry-packed 1.5 kg silica gel 60 (EM laboratories, 70–230 mesh) columns. Elution with carbon tetrachloride brought the isothiocyanate through close behind the solvent front.

The various phosphates seem to stay near the origin under these conditions and it has been possible to reuse these columns for as many as three runs. This partially purified product (21 g) was rechromatographed on a fresh column (1.5 kg) and 15.8 g (11%) of pale yellow oil was obtained on distillation at 44 °C (0.4 mm). The sample for elemental analysis was prepared by gas chromatography on a Hewlett-Packard 5750 preparative GC, using a 12 ft × 0.5 in. 10% QF-1 column, carrier flow rate 80 mL/min, oven temperature 150 °C, retention time 10 min: NMR (CCl_4) δ 6.63–7.01 (m, 3 H, thienyl H).

Anal. Calcd for $C_5H_3NS_2$: C, 42.53; H, 2.14: N, 9.92; S, 45.41. Found: C, 42.50; H, 2.11; N, 9.75; S, 45.49.

3-Thienyl Isothiocyanate (6). **4** (15 g, 48 mmol) was heated at 18 mm pressure in an oil bath maintained at 135–140 °C until distillation stopped. The distillate was chromatographed on 50 g of silica gel 60 (EM Laboratories, 70–230 mesh) and eluted with carbon tetrachloride, then distilled on a Nester-Faust Teflon spinning band column yielding 2.28 g (34%) of a yellow oil: bp 98–99 °C; NMR (CCl_4) δ 6.87 (q, 1, 4-H), 7.02 (q, 1, 2-H), 7.20 (q, 1, 5-H); $J_{2,4}$ = 1.4, $J_{2,5}$ = 3.1, $J_{4,5}$ = 4.8 Hz; n^{25}_D 1.6771.

Anal. Calcd for $C_5H_3NS_2$: C, 42.53; H, 2.14; N, 9.92; S, 45.41. Found: C, 42.67; H, 2.00; N, 10.05; S, 45.27.

***N*-*n*-Propyl-*N'*-(2-thienyl)thiourea (9).** *n*-Propylamine (0.7 g, 12 mmol) was added to a solution of 0.4 g (2.8 mmol) of **5** in 10 mL of carbon tetrachloride and the mixture was stirred for 20 min. The solvent and excess amine were partially evaporated and the solid product was recrystallized from carbon tetrachloride–petroleum ether, 480 mg (85%) of white plates: mp 100.0–100.5 °C; NMR ($CDCl_3$) δ 0.88 (t, 3, CH_3), 1.59 (sextet, 2, CCH_2C), 3.58 (t, 2, NCH_2), 6.23 (br band, 1, RNH), 6.78 (m, 1, 3-H), 6.90 (m, 1, 4-H), 7.15 (q, 1, 5-H), 8.27 (br s, 1, thienyl NH); NMR (acetone-d_6) δ 0.88 (t, 3. CH_3), 1.59 (sextet, 2, CCH_2C), 3.52 (q, 2, NCH_2), 6.73 (q, 1, 3-H), 6.82 (q, 1, 4-H), 7.03 (q, 1, 5-H), ca. 7.22 (partially obscured by the 5-H) (br band, 1, RNH), 9.27 (br s, 1, thienyl NH); $J_{3,4}$ = 3.7, $J_{3,5}$ = 1.7, $J_{4,5}$ = 5.3, J_{CH_2,CH_3} = 7.5, J_{CH_2,CH_2} = 6.4 Hz.

Anal. Calcd for $C_8H_{12}N_2S_2$: C, 47.96; H, 6.04: N, 13.99; S, 32.01. Found: C, 48.16; H, 5.95; N, 13.91; S, 31.87.

***n*-Propyl *N*-(2-Thienyl)thionecarbamate (13).** A solution of 420 mg (3.0 mmol) of **5** and 1.6 g (27 mmol) of dried *n*-propyl alcohol in 15 mL of *n*-heptane was heated under reflux for 18 h. The mixture was partially evaporated to yield a white solid, 485 mg (80%), mp 46.0–48.5 °C. The analytical sample was vacuum sublimed, white needles: mp 48.0–48.5 °C; NMR ($CDCl_3$) δ 1.02 (t, 3, CH_3), 1.83 (sextet, 2, CCH_2C), 4.39 (t, 2, OCH_2), 6.70–7.03 (m, 3, thienyl H), 9.99 (br band, 1, NH); J_{CH_2,CH_3} = 7.5, J_{CH_2,CH_2} = 6.5 Hz.

Anal. Calcd for $C_8H_{11}NOS_2$: C, 47.73; H, 5.51; N, 6.96; O, 7.95; S, 31.86. Found: C, 47.66; H, 5.56; N, 7.03; O, 8.03; S, 32.00

***tert*-Butyl *N*-(2-Thienyl)thionecarbamate (15).** A stirred slurry of potassium *tert*-butoxide (895 mg, 7.1 mmol) in sodium-dried tetrahydrofuran was heated under reflux with 1.0 g (7.1 mmol) of **5** for 1 h under anhydrous conditions, 0.25 mL of water was added, and heating was continued for 15 min. The mixture was cooled to room temperature and 1 mL of 6 N hydrochloric acid was added with stirring. The precipitate of potassium chloride was filtered and the solution was evaporated to a small volume. Upon adding distilled water, an oil separated and crystallized on standing. The product was recrystallized from petroleum ether to yield 760 mg (49%) of light brown crystals, mp 95–96 °C dec. The analytical sample was vacuum sublimed to produce white crystals: mp 92.5–93.5 °C dec; NMR (acetone-d_6) δ 1.77 (s, 9, CH_3), 6.80–7.08 (m, 3, thienyl H), 10.57 (br band, 1, NH).

Anal. Calcd for $C_9H_{13}NOS_2$: C, 50.20; H, 6.08; N, 6.51; O, 7.43; S,

29.78. Found: C, 50.12; H, 6.13; N, 6.41; O, 7.58; S, 29.69.

***tert*-Butyl *N*-(2-Thienyl)dithiocarbamate (19).** A slurry of lithium *tert*-butylmercaptide (682 mg, 7.1 mmol), **5** (1.0 g, 7.1 mmol), and 10 ml of *tert*-butyl mercaptan was heated under reflux for 5 min and then stirred at room temperature in a foil-covered flask for 20 h under anhydrous conditions. The mercaptan was evaporated under a stream of nitrogen and the pasty residue was neutralized with hydrochloric acid. The resultant oil was extracted with ether and evaporation of the ether gave a crystalline product. This was chromatographed on a dry-packed 40 g silica gel 60 (EM Laboratories, 70–230 mesh) column and eluted with carbon tetrachloride. Unreacted 2-thienyl isothiocyanate comes with the solvent front and the product comes a little later. The product was recrystallized from petroleum ether with decolorization by acid-washed Norit A charcoal, yielding 1.42 g (86%) of yellow needles: mp 87.5–88.5 °C dec; NMR (CCl_4) δ 1.63 (s, 9, CH_3). 6.80–7.01 (m, 3, thienyl H), 9.17 (br band, 1, NH).

Anal. Calcd for $C_9H_{13}NS_3$: C, 46.71; H, 5.66; N, 6.05; S, 41.57. Found: C, 46.82; H, 5.56; N, 6.06; S, 41.72.

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Registry No.—**1**, 2046-39-1; **3**, 61528-47-0; **4**, 61528-48-1; **5**, 61528-49-2; **6**, 61528-50-5; **7**, 61528-51-6; **8**, 61528-52-7; **9**, 61528-53-8; **10**, 61528-54-9; **11**, 61528-55-0; **12**, 51460-50-5; **13**, 61528-56-1; **14**, 61528-57-2; **15**, 61528-58-3; **16**, 61528-59-4; **17**, 61528-60-7; **18**, 61528-61-8; **19**, 61528-62-9; *O,O'*-diethylhydrogen dithiophosphate, 298-06-6; 3-thenoyl azide, 59445-89-5; propylamine, 107-10-8; propyl alcohol, 71-23-8; potassium *tert*-butoxide, 865-47-4; *tert*-butyl mercaptan, 75-66-1.

Supplementary Material Available. Chemical analyses and NMR data for the compounds listed in Table I (3 pages). Ordering information is given on any current masthead page.

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Thiocyanations. 2. Solvent Effects on the Product Distribution of the Thiocyanogen–Olefin Reaction

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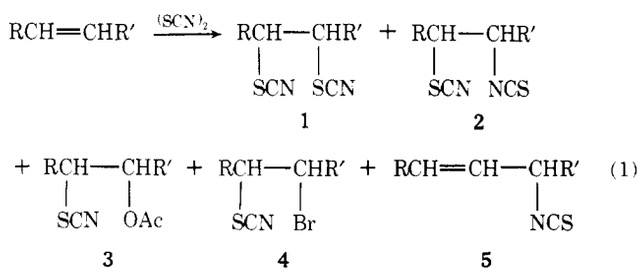
The heterolytic addition of thiocyanogen to *cis*- and *trans*-3-hexene has been carried out in a variety of solvent systems. Unlike ionic bromine addition to aliphatic olefins, this pseudohalogen reaction can yield either adduct **1** or **2** as the principal product dependent on the type of solvent employed. Dithiocyanates (**1**) are preferentially formed in polar and dipolar aprotic media, whereas isothiocyanatothiocyanates (**2**) become the principal products in nonpolar solvents. It was also observed that the product outcome was significantly altered when iron powder or ferric thiocyanate was added to the reaction medium. The effects of solvents and iron on the product composition are explicable through the Pearson HSAB concept. The free-radical thiocyanation reaction was also examined and the results are briefly discussed.

Thiocyanogen addition to alkyl olefins is a well-known procedure[3] for the preparation of α,β-dithiocyanates **1** as well as a classical analytical method for determination of the unsaturation in fats and oils. The reaction, traditionally carried out in acetic acid, had been known to yield only the adducts **1**[4] until the recent isolation of the isomeric α-isothiocyanato-β-thiocyanate **2** and ancillary coproducts **3–5** (eq 1).[5]



(1)

trans olefin → erythro (meso) (**1a–4a**)
cis olefin → threo (*dl*) (**1b–4b**)

Quantitation of product distribution has only been reported for reactions carried out in acetic acid solution.[5] Although adduct **2** has also been identified as a coproduct in benzene and carbon tetrachloride solution reactions, the extent of its formation relative to adduct **1** had not been ascertained.[6] Since adducts **1** and **2** have recently found use as synthetic intermediates,[7] a need existed for an improved method of selective conversion of olefins to either **1** or **2**.

The present investigation was initiated to determine the influence of various reaction parameters on the composition of the product mixture, since only limited information was available in the literature.[3b,6] A specific aim of this work was to determine the influence of solvent variation on the product distribution. A quantitative examination of the addition reaction was also carried out under irradiative conditions to compare the products formed by ionic and free-radical pathways. It was anticipated that an understanding of the solvents' role in determining the products formed from thiocyanogen additions would aid in clarification of the mechanism of addition of this ambident pseudohalogen to olefins.

Results

The present study was implemented with *cis*- and-*trans*-3-hexene as convenient model olefins[8] for which the products were easily analyzed by GLC. Earlier studies in this laboratory[5] have indicated that the product outcome is not influenced by the chain length and hence it was anticipated that the results obtained on 3-hexene could be projected to longer