The Nature of the Carbonium Ion. II. The Furfuryl Cation from a Thiocyanate–Isothiocyanate Isomerization

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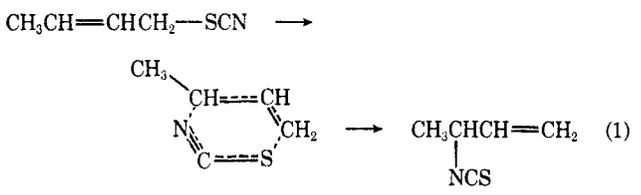
In contrast to the essentially irreversible isomerizations of most alkyl thiocyanates, including benzyl, the isomerization of furfuryl thiocyanate was discovered to proceed to an equilibrium position in which a substantial amount of the starting material was still present. The second component at equilibrium, furfuryl isothiocyanate, was always predominant, but relative proportions at equilibrium were strongly solvent influenced. Examination of the equilibrium position over a large temperature span revealed an almost negligible temperature dependence in a given solvent. Measurements of the rates of reaction in several solvents showed the isomerization to be in all cases a first-order process but accelerated by the more nucleophilic solvent, dimethylformamide. A comparison of activation parameters for forward and reverse reactions revealed that the favoring of isothiocyanate at equilibrium is based only on a slightly more favorable activation entropy for the forward reaction.

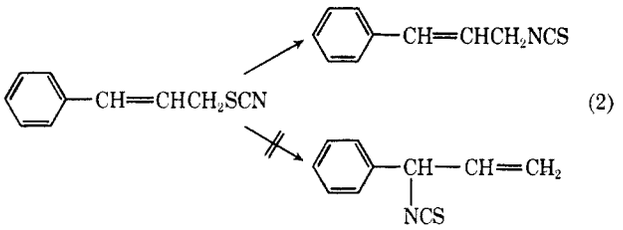
Allylic and benzylic thiocyanate isomerizations have been more intensively investigated than those of saturated thiocyanates.[1,2] This is probably due to the greater ease with which most of the unsaturated systems undergo transformation to isothiocyanates. In the preceding paper of this series[3] we demonstrated that even a remote double bond can produce a drastic increase in the rate of isomerization because of its participation in the initial ionization process. Nonetheless, a uniform mechanistic picture for all unsaturated isomerizations cannot be presented. This becomes obvious when one notes that allylic compounds appear to isomerize at rates much faster than would seem warranted by their relative electron-releasing abilities.[1a,2] The reason for this discrepancy lies in the availability to allylic thiocyanates of a cyclic intramolecular pathway for isomerization which is not possible for nonallylic compounds. This means of conversion, first suggested by Billeter,[4] was supported by Mumm and Richter[5] in their observation that crotyl thiocyanate gives α-methylallyl isothiocyanate (eq 1)



(1)

upon heating. Results from examination of the kinetics of several allylic isomerizations by Smith and Emerson[2a] and by Iliceto and Fava[1a] have subsequently provided confirmation of this fact.

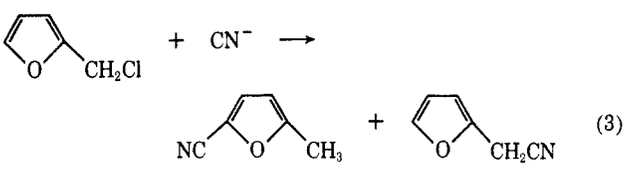
Even allylic thiocyanates do not provide a completely consistent mechanistic picture, however. For example, cinnamyl thiocyanate fails to give allylic rearrangement upon isomerization[2a] (eq 2). The sole



(2)

product, cinnamyl isothiocyanate, points out the inconsistency not only by its unrearranged carbon skeleton, but also by the sluggishness of its formation relative to other allylic isothiocyanates.[2a] In this instance, the allylic shift is opposed by the resulting loss of conjugation in the α-phenylallyl group.[6] Dissociation to the cinammyl cation and thiocyanate ion therefore becomes the favored pathway for isomerization.

The energy borderline separating the two types of allylic isomerization is, in consequence, of some interest. In an effort to investigate this energy borderline, the furfuryl system was chosen for study. This system appeared promising since in contrast to the cinnamyl system several reports are to be found where disruption of the conjugated nucleus is suspect (if not confirmed) by displacements on furfuryl derivatives.[8,9] The reaction of cyanide ion with furfuryl chloride, giving mainly 5-cyano-2-methylfuran (eq 3), appears to be the



(3)

best documented example of this kind.[8,9] The "abnormal" product is probably derived from an intermediate species in which the furan structure is temporarily rearranged. This sort of intermediate has in fact recently been isolated from the reaction of furfuryl

(1) (a) A. Iliceto, A. Fava, and U. Mazzucato, *Tetrahedron Lett.*, **No. 11**, 27 (1960); (b) A. Iliceto, A. Fava, U. Mazzucato, and P. Radici, *Gazz. Chim. Ital.*, **90**, 919 (1960); (c) A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *J. Amer. Chem. Soc.*, **83**, 2729 (1961); (d) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *ibid.*, **87**, 1045 (1965); (e) A. Fava, A. Iliceto, and S. Bresendola, *ibid.*, **87**, 4791 (1965); (f) A. Fava, U. Tonellato, and L. Congin, *Tetrahedron Lett.*, 1657 (1965).

(2) (a) P. A. S. Smith and D. W. Emerson, *J. Amer. Chem. Soc.*, **82**, 3076 (1960); (b) D. W. Emerson and J. K. Booth, *J. Org. Chem.*, **30**, 2480 (1965).

(3) L. A. Spurlock and W. G. Cox, *J. Amer. Chem. Soc.*, **91**, 2961 (1969).

(4) O. Billeter, *Helv. Chim. Acta*, **8**, 337 (1925).

(5) O. Mumm and H. Richter, *Ber.*, **73**, 843 (1940).

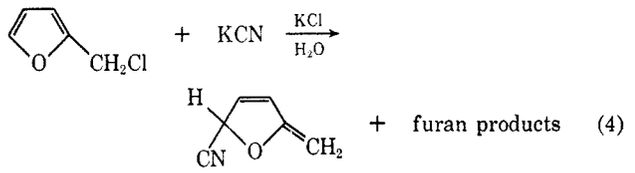
(6) An attempt at preparation of α-phenylallyl isothiocyanate from α-phenylallyl amine and carbon disulfide gave only cinammyl thiocyanate.[7]

(7) A. Iliceto and G. Gaggia, *Gazz. Chim. Ital.*, **90**, 262 (1960).

(8) For a summary see A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953, pp 230–251.

(9) (a) O. Moldenhauer, G. Trautmann, and R. Pflueger, *Ann. Chem.*, **583**, 61 (1953); (b) C. Y. Benning, Ph.D. Thesis, Ohio State University, 1953; *Diss. Abstr.*, **18**, 1612 (1958); (c) J. Egyed and A. Gerecs, *Acta Chim. Acad. Sci. Hung.*, **29**, 91 (1961).

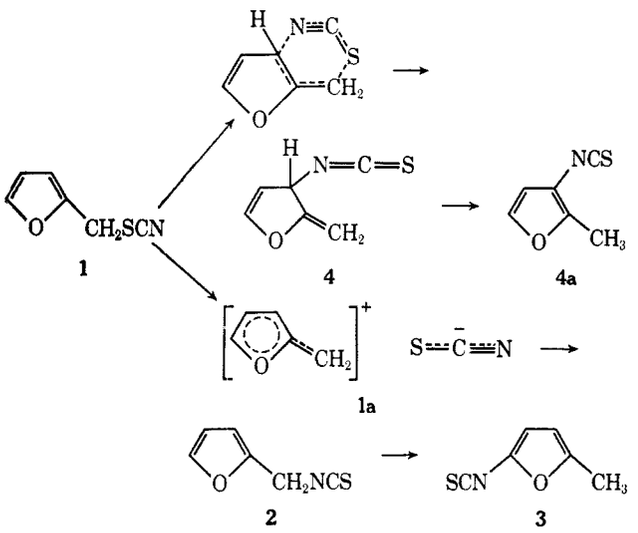
chloride with potassium cyanide in aqueous potassium chloride solution[10] (eq 4).



+ furan products (4)

Corresponding attack on the 3 position of furan has not yet been observed, but it would not seem unreasonable to anticipate its occurrence under proper circumstances. With this latter thought in mind, the prospective competing processes occurring during isomerization of furfuryl thiocyanate (**1**) (see Scheme I) would appear to afford excellent opportunity for evaluation of the importance of attack at C_3 (and at C_5). The degree of allylic and/or aromatic behavior by the

SCHEME I



furfuryl moiety during isomerization is thus of interest for several reasons.

Results

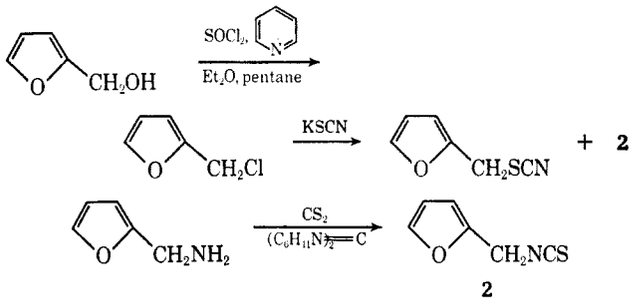
The synthesis of furfuryl thiocyanate[9a] (**1**) was accomplished utilizing the displacement by thiocyanate ion on furfuryl chloride or furfuryl *p*-toluenesulfonate in anhydrous acetone solution. Not surprisingly[11] no "abnormal" 5- or 3-substituted isomers were detected in the product mixture. The mixture, as analyzed by infrared and nmr, consisted of thiocyanate **1** and its isomer, furfuryl isothiocyanate (**2**), in a 77:23 ratio (Scheme II). Separation of pure thiocyanate **1** was accomplished either *via* chromatography on silica gel, or by conversion of the isothiocyanate **2** into its thiourea derivative with *t*-butylamine, followed by fractional distillation. An authentic sample of pure **2** was prepared also by treatment of furfurylamine with dicyclohexylcarbodiimide and carbon disulfide in anhydrous ether (Scheme II). Structural assignments and purity in excess of 98% could be confirmed by nmr analysis for both compounds. (See Experimental Section.)

(10) M. M. Joullié, private communication.

(11) The reaction of potassium cyanide with furfuryl chloride in dimethylformamide similarly gave no "abnormal" product.[12]

(12) K. Yu. Novitskii, Kh. Gresl', and Yu. K. Yur'ev, *Zh. Org. Khim.*, **1** 539 (1965).

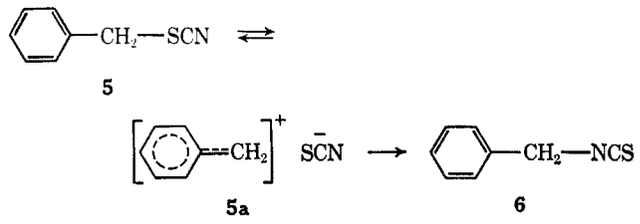
SCHEME II



Isomerizations of **1** were initially undertaken in refluxing acetonitrile solutions of moderate dilution (0.1 *M*). Nmr analyses of the product mixtures indicated that only one isothiocyanate, **2**, was formed. Further, the isomerization could be shown as a measurable equilibrium process by the observation that beginning with pure thiocyanate **1**, or pure isothiocyanate **2**, the same steady product composition was ultimately attained. The rates of isomerization could be demonstrated as first-order processes beginning with **1** or **2**. The effects of temperature on the equilibrium position and rates of isomerization were therefore examined and activation parameters calculated. (See Table I.) Analysis was accomplished by periodically quenching aliquots being held at constant temperature, followed by measurements of the relative areas of nmr absorption peaks due to the methylene protons of **1** (τ 5.78) and **2** (τ 5.33). Equilibrium values reported are the averages of at least two runs with material recovery 90–95%, and rate constants are the average values for at least three runs.

The peculiar relationships of equilibrium compositions and rates in acetonitrile and sulfolane to those in dimethylformamide dictated a more extensive investigation of solvent effects. The combined results of equilibrium studies are tabulated in Table II. The values reported are likewise the averages of at least two runs. Isomerizations of both **1** and **2** were also effected in cyclohexane solution; however, equilibrium was not attained in either case after 89 hr of heating at 150°. Decomposition was prevalent at this point; therefore, equilibration was not sought further.

As a basis of comparison for the previous results the isomerization of benzyl thiocyanate (**5**) was also subjected to study. Commercial **5** was found to be satisfactory for these purposes. An authentic sample of benzyl isothiocyanate (**6**) was prepared by the method of Jochims and Seeliger.[13] Purity in excess of 99% could be confirmed for both compounds by gc analysis.



Isomerizations of **5** were attempted using conditions closely approximating those utilized in studies of **1**. It was found, in sharp contrast to **1**, that **5** does not

(13) J. C. Jochims and A. Seeliger, *Angew. Chem.*, **6**, 174 (1967).

TABLE I

ISOMERIZATIONS OF FURFURYL THIOCYANATE (1) AND ISOTHIOCYANATE (2)

Starting material	Solvent	Temp, °C	RNCS at equil, %	RSCN at equil, %	$10^5 \times k$ sec^{-1}	K_{eq}[a]	$t_{1/2}$, hr
RSCN[d]	CH_3CN	81	80.1 ± 0.03	19.9	1.85 ± 0.03		8.3
						4.1	
RNCS[e]			80.8 ± 0.2	19.2	0.46 ± 0.03[b]		
RSCN		101	79.7 ± 0.2	20.3	16.8 ± 0.3		0.91
						4.0	
RNCS			80.1 ± 0.2	19.9	4.28 ± 0.5[b]		
RSCN		120	81.0 ± 0.4	19.0	71.5[c]		0.22
						4.1	
RNCS			80.0 ± 0.1	20.0	16.8[b]		
RSCN	DMF	81	85.2 ± 0.8	14.8	14.7 ± 0.8		1.1
						5.8	
RNCS			85.3 ± 0.1	14.7	2.55 ± 0.07[b]		
RSCN	Sulfolane		80.7 ± 0.3	19.3	7.71 ± 0.16		
						4.1	
RNCS			79.9 ± 0.3	20.1	1.94 ± 0.07		2.0

[a] Averaged from forward and reverse results. [b] Calculated from experimentally determined value for reverse reaction. [c] Estimated from one run. [d] RSCN: $\Delta H^{\ddagger} = 29$ kcal/mol; $\Delta S^{\ddagger}_{81^\circ} = +1.3$ eu. [e] RNCS: $\Delta H^{\ddagger} = 29$ kcal/mol; $\Delta S^{\ddagger}_{81^\circ} = -1.8$ eu.

TABLE II

EFFECTS OF SOLVENT ON EQUILIBRIUM COMPOSITIONS FROM FURFURYL THIOCYANATE AND ISOTHIOCYANATE

Starting material	Solvent	Temp, °C	RNCS at equil, %	RSCN at equil, %	$t_{1/2}$, hr
RSCN	C_6H_6	150	89.5 ± 0.6	10.5	8.3
RNCS			89.4 ± 0.6	10.6	
RSCN	$CHCl_3$	150	85.5 ± 0.1	14.5	5.5
RNCS			85.3 ± 0.3	14.7	
RSCN	$CH_3CO_2C_2H_5$	150	85.8 ± 0.2	14.2	3.6
RNCS			85.3 ± 0.2	14.7	
RSCN	CH_3COCH_3	150	83.7 ± 0.2	16.3	2.8
RNCS			83.2 ± 0.2	16.8	
RSCN	CH_3CN	141	80.7 ± 0.2	19.3	0.13
RNCS			79.7 ± 0.3	20.3	
RSCN	Sulfolane	81	80.7 ± 0.3	19.3	2.0
RNCS			79.9 ± 0.3	20.1	
RSCN	DMF	81	85.2 ± 0.8	14.8	1.1
RNCS			85.3 ± 0.1	14.7	

isomerize to any measureable extent for 24 hr at 120° when acetonitrile is the solvent. Use of sulfolane afforded observable isomerization, but conversion into **6** was only to the extent of 9.6% after 24 hr at 150°. A third solvent, N-methylpyrrolidone, was also utilized and found to cause a larger conversion into isothiocyanate **6**, but side products and decomposition prevented accurate assessments of relative amounts. No "reverse" isomerization of **6** into **5** could be detected under any conditions.

Discussion

The greatly enhanced reactivities of the furfuryl derivatives, **1** and **2**, over those of their benzyl counterparts, **5** and **6**, are more comprehensible if considered in light of the relative instabilities of the furfuryl halides[14] as compared with benzyl halides. In the furfuryl cases unimolecular dissociation routes giving ions similar to **1a** are clearly more favorable energetically than the comparable dissociations of benzyl compounds to ions like **5a**. Indeed, a comparison with the isomerization of benzhydryl thiocyanate[1c] reveals that **1** isomerizes more slowly than this reactive thiocyanate only by a factor of 5, at 80° in acetonitrile. The rapid isomerization of **1** would seem to be couched in its ease of dissociation to the furfuryl cation rather than in an allyl-type cyclic pathway to isomerization. Prospects for this latter process occurring in isomerizations of **1** and **2** (see Scheme 1) are considerably dimmed by the failure to observe **4a** or any other 3-substituted product. That allylic shift transient species cannot be involved is supported by thermodynamic arguments based on the observed temperature insensitivity of equilibrium position. A further indication of this was obtained from continuous monitoring of the isomerization by nmr. This was accomplished using a time-averaging computer and heated probe. No evidence for the existence of **4** or its thiocyanate counterpart could be found despite the rather sensitive means of detection. In addition, the strong solvent influence on the rate of isomerization is more typical of reactions where ions are generated from neutral reactants than of cyclic processes involving little charge separation. The isomerizations of most allylic thiocyanates do reflect their cyclic nature by their relative solvent insensitivity.[1a,2]

The unusual observation that equilibration of **1** and **2** proceeded, respectively, eight and four times more slowly in acetonitrile and sulfolane than in dimethylformamide indicates that the role of dimethylformamide may be somewhat different from those of other solvents.

(14) Furfuryl chloride was found to explode violently when stored neat at 0°. (See Experimental Section.)

Our own studies[3,15] of alkyl thiocyanate isomerizations have revealed the general relation of solvent to reactivity as follows: sulfolane > acetonitrile ≈ dimethylformamide. In all these cases, however, backside approach by solvent on the reaction site is unlikely, and in most cases sterically prohibited. Since this is not the case with **1** or **2**, nucleophilicity of the solvent may bear an increased responsibility in rate influences. Thus the known[16] nucleophilic tendencies of dimethylformamide, in contrast to the at best very weakly nucleophilic characteristics of most of the other solvents employed, can be held responsible for the unusual reactivity relationship. Evidence was sought for an intermediate species incorporating both dimethylformamide and the furfuryl group to provide confirmation of direct participation. No sign of its existence could be detected through attempts at isolation or by nmr observations. This does not rule out direct assistance by dimethylformamide but indicates that collapse into **2** or **1** must occur prior to formation of a full furfuryl–dimethylformamide bond.

The unusual aspect of these isomerizations is the observable reverse change of isothiocyanate to thiocyanate. This is not without precedent since Iliceto and Fava[1a] had reported that a few allylic thiocyanates showed isomerizations to equilibrium positions in which measurable amounts of thiocyanate were detectable. The proportion of thiocyanate at equilibrium was found to be larger in acetonitrile than in cyclohexane and so was attributed to the greater ability of the more polar solvent to stabilize the larger dipole associated with the thiocyanate group.[1a] In most of these cases, however, the additional driving force of a more stable carbon skeleton for the thiocyanate was also present due to the allylic shift during isomerization. Benzhydryl thiocyanate, the lone nonallylic compound reported to give a detectable thiocyanate concentration at equilibrium, did so only in acetonitrile and in a percentage (2–3%) barely above the limits of detection.[1a] The equilibrium position of the two furfuryl compounds indicates therefore the greatest thermodynamic equivalence between thiocyanate and isothiocyanate yet observed. The reason for this peculiarity must necessarily be a matter of conjecture. It nevertheless seems appropriate to note that the furan ring, being more polarizable than the completely aromatic benzene nuclei of benzyl and benzyhydryl and certainly more polarizable than the σ bonds of most alkyl thiocyanates, may account for the enhanced stability of the sulfur-bound thiocyanate relative to the nitrogen-bound species. This same theory is applicable to the unsubstituted and 2-methylallyl examples since here allylic shift gives the identical carbon skeleton and the greater attraction of the π bond for the more polarizable, "soft" sulfur end of thiocyanate can be invoked to explain the seeming anomaly of detection of thiocyanate at equilibrium.

The effect of solvent on equilibrium position was essentially as to be expected if the reasoning applied to the allylic equilibria is accepted.[17] Certainly the equilibrium does appear to parallel solvent polarity with the exception of the previously discussed dimethylformamide. A linear relationship was discovered by plotting the logarithms of the solvent dielectric constants *vs.* the fraction of thiocyanate present at equilibrium. Admittedly this is of limited significance due to the necessary assumption that the relationships of dielectric constants at 20° (where most of the dielectrics were measured) are identical with those at 150° (where most of the equilibria were examined). This is however an indication that nonpolar and polar solvents, except dimethylformamide, influence the equilibrium by the same principal means, and that solvation of the ground states of the isomers may indeed be important to the position of equilibrium.

The almost negligible temperature influence on the equilibrium position over a span of 60° (see Tables I and II) in acetonitrile illustrates the nearly identical activation enthalpies of the forward and reverse reactions. The more rapid attainment of equilibrium starting with the thiocyanate is primarily the result of a more favorable activation entropy for the forward (thiocyanate to isothiocyanate) reaction. Explanation for this entropy difference probably lies in the lesser extent of solvent shell reorganization required by the more polar thiocyanate and upon ionization as compared with that required by the less polar isothiocyanate.

A final point worth mentioning is the failure to observe any products of attack at the 5 position of the furfuryl cation. As all prior observations[3,9] of attack at this position had occurred only in very polar solvents (methanol, water, dioxane–water), this result is not extraordinary. Nonetheless it does lend further support to the theory which we advanced in the preceding paper[3] that the thiocyanate ion, once generated by dissociation, shows a marked tendency to collapse onto the site to which it was originally attached before migration to other electron-deficient centers is possible. Further examination of this phenomenon will be reported in subsequent papers of the series.

Experimental Section[18]

Furfuryl *p*-Toluenesulfonate.—To a solution of 9.8 g (0.10 mol) of furfuryl alcohol in 24.2 g (0.20 mol) of *s*-collidine was added 19.1 g (0.10 mol) of recrystallized *p*-toluenesulfonyl chloride in small portions over a 15-min period. The temperature was maintained below 20° with continuous stirring. To this mixture was added 20 ml of methylene chloride and stirring was continued at 10° for an additional 1.75 hr. A 25-ml portion of cold 2.5 *N* sulfuric acid was then added and the organic layer was separated, extracted with two 13-ml portions of cold sulfuric acid, neutralized with granular potassium carbonate, and then filtered through magnesium sulfate. The filtrate was concentrated giving 10.1 g (40.1%) of crude ester, as a red oil which decomposed on standing open to the atmosphere. A small portion of the crude ester was dissolved in anhydrous ether; the solution was filtered and the filtrate evaporated under dry nitrogen. This procedure gave a white crystalline solid which immediately decomposed to the atmosphere: ir (mull) 1360 and 1170 cm^{-1}.

(15) L. A. Spurlock and P. E. Newallis, *Tetrahedron Lett.*, 303 (1966); L. A. Spurlock and T. E. Parks, unpublished results.

(16) D. R. Dalton, *et al.*, Division of Organic Chemistry, Paper 9, 4th Middle Atlantic Regional Meeting of the American Chemical Society, Washington, D. C., Feb 1969; F. C. Chang and R. T. Blickenstaff, *J. Amer. Chem. Soc.*, **80**, 2906 (1958).

(17) The order of elution (isothiocyanate prior to thiocyanate) from silica gel columns and all gc columns utilized would seem to support this.

(18) Infrared spectra were determined with a Perkin-Elmer Infracord using sodium chloride optics. The nmr determinations were carried out on a Varian Associates A-60A spectrometer; approximately 20% solutions in CCl_4 were employed with tetramethylsilane as the internal standard. Analyses were carried out by Micro-Analysis, Inc. of Wilmington, Del. All solvents used were commercial anhydrous reagent grade materials. The sulfolane was redistilled from potassium permanganate under nitrogen.

The crude ester was found to be satisfactory for use in displacement reactions.

Furfuryl chloride was prepared as described by Kirner, Reichstein, and Moldenhauer,[19] in 53–73% yield: bp 52–53° (31 mm) [lit.[19] bp 53–53.5° (32 mm)]; infrared spectrum (neat) 1500, 1265, 1155, 1072, 1018, 944, 745, and 693 cm^{-1}. [Note: It was found that this chloride, if not distilled directly into a solvent, undergoes a violent explosion with evolution of hydrogen chloride fumes. Therefore, it was distilled directly into anhydrous acetone and the solution stored in the cold for further use.]

Furfuryl thiocyanate (1) was prepared by allowing 20.0 g (0.172 mol) of furfuryl chloride to react with 23.3 g (0.241 mol) of potassium thiocyanate in 50 ml of anhydrous acetone. After 18 hr of stirring at ambient temperature, the potassium chloride was removed by filtration and washed with a minimum amount of acetone. Concentration of the filtrate and acetone washings, followed by a distillation, bp <60° (0.05 mm), afforded 20.5 g of impure furfuryl thiocyanate. The impure material, shown by nmr to be contaminated with approximately 23% of **2**, was added to a solution of 3.0 g (0.041 mol) of *t*-butylamine in 50 ml of anhydrous ether and stirred for 2 hr.[20] The mixture was concentrated and distillation of the residue gave 7.6 g (31.8%) of colorless product: bp 46–48° (0.05 mm) [lit.[9a] bp 106° (14 mm)]; $n^{25}D$ 1.5411 (lit.[21] $n^{20}D$ 1.5419); infrared spectrum (neat) 2160, 1500, 1245, 1155, 1070, 1014, 940, and 745 cm^{-1}; nmr (CCl_4) τ 2.55 (dd), 3.53–3.71 (m), and 5.78 (s).

Anal. Calcd for C_6H_5NOS: C, 51.78; H, 3.62; N 10.06; S, 23.04. Found: C, 52.02; H, 3.62; N, 10.23; S, 22.64.

Furfuryl Isothiocyanate (2) was prepared using the procedure described by Jochims and Seeliger.[13] A solution of 9.7 g (0.10 mol) of furfurylamine (Aldrich Chemical Co.) in 20 ml of dry ether was added dropwise to a stirred solution of 40 ml of carbon disulfide, 20.6 g (0.10 mol) of dicyclohexylcarbodimide, and 200 ml of dry ether, maintaining the temperature at −10°. When the addition was completed the temperature was allowed to rise to room temperature during a 3-hr period. After 18 hr of stirring, the dicyclohexylthiourea was removed by filtration and washed with ether. Concentration of the filtrate and ether washings, followed by distillation at 47–50° (0.6 mm), afforded 10.1 g (72.6%) of furfuryl isothiocyanate; $n^{25}D$ 1.5616 [lit.[2] $n^{20}D$ 1.5630]; infrared spectrum (neat) 2070–2150, 1330, 1145, 1012, 910, and 745 cm^{-1}; nmr spectrum (CCl_4) τ 2.60 (tr), 3.64 (d), and 5.33 (s).

Anal. Calcd for C_6H_5NOS: C, 51.78; H, 3.62; N, 10.06; S, 23.04. Found: C, 51.87; H, 3.56; N, 10.10; S, 22.60.

1-(Furfuryl)-3-*t*-butylthiourea. A solution of 1.000 g (13.6 mmol) of *t*-butylamine and 1.000 g (7.18 mmol) of furyl isothiocyanate in 50 ml anhydrous ether was allowed to stand overnight at ambient temperature. The reaction mixture was concentrated giving a dark oily residue, which was passed through a 6 × 0.5 in. silica gel column using anhydrous ether as the eluent. The ether solution was concentrated giving a dark oil, which solidified on standing. Purification was accomplished by treatment with activated charcoal and recrystallization twice from ether–pentane. This afforded 0.840 g (55.3%) of a yellowish white crystalline solid: mp 70.5–71.5°; infrared spectrum (mull) 3250, 3050, 2930, 1525, 1390, 1350, 1290, 1190, 1145, 1075, 1010, 885, and 739 cm^{-1}; nmr (CCl_4) τ 2.95 (tr), 3.65 (br, tr), 3.80 (br. s), 3.86–4.04 (mult), 5.50, 5.59 (d), and 8.65 (s).

Anal. Calcd for $C_{10}H_{16}N_2S$: C, 56.57; H, 7.60; N, 13.19; S, 15.10. Found: C, 56.81; H, 7.58; N, 13.14; S, 14.99.

Benzyl Isothiocyanate (6) was prepared as described by Jochims and Seeliger[13] in 75.8% yield: bp 67° (0.025 mm) [lit.[13] 125–126° (12 mm)]; infrared spectrum (neat) 2990, 2890, 2100, 1600, 1490, 1450, 1430, 1340, 1025, and 700 cm^{-1}; nmr spectrum (CCl_4) τ 2.64 (s) and 5.35 (s).

Isomerizations of 1 and 2.—Solutions 0.100 *M* in **1** and **2** were prepared using cyclohexane, benzene, chloroform, ethyl acetate, acetone, and acetonitrile. Aliquots (7 ml) were sealed in glass tubes and heated for various amounts of time.[22] The contents of the tubes were concentrated, dissolved in carbon tetrachloride which was 2% in tetramethylsilane, and transfered to nmr tubes. The solutions were scanned in the τ 4.40–6.0 region to analyze for relative amounts of **1** and **2**. Solutions in dimethylformamide and sulfolane were prepared and sealed into tubes as mentioned above. The contents of the tubes were removed after heating and poured into 50 ml of water. Extraction with three 20-ml portions of ether, followed by washing the combined extracts with three 20-ml portions of water, drying, and concentrating, gave mixtures of **1** and **2**. These were analyzed as above.

Isomerization of 5.—Solutions 0.100 *M* in **5**[23] were prepared using sulfolane, acetonitrile, and N-methylpyrrolidone. These were sealed in glass tubes, heated at 120 or 150° for 27 hr, and worked-up as mentioned before. Mixtures were analyzed by scanning the τ 5.0–6.0 region in the nmr spectrum and measuring the relative areas of absorption peaks at τ 5.80 (**5**) and 5.35 (**6**).

Kinetic Procedure.—Aliquots (7 ml) of acetonitrile solution 0.100 *M* in **1** or in **2** were sealed in glass tubes and heated at 81.0, 101.0, or 120.0°. The tubes were removed at various intervals and quenched by immersion in ice. The resultant solutions were concentrated and the residues dissolved in carbon tetrachloride which was 2% in tetramethylsilane. Analysis was accomplished by scanning the τ 4.0–6.0 region of the nmr spectrum and measuring the relative areas of absorption peaks at τ 5.78 (**1**) and 5.33 (**2**). A similar procedure was utilized for kinetic studies in dimethylformamide and sulfolane. The work-up of these samples has been mentioned previously.

Registry No.—**1**, 4650-59-3; **2**, 4650-60-6; furfuryl *p*-toluenesulfonate, 19820-73-6; 1-furfuryl-3-*t*-butyl thiourea, 21690-83-5.

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(19) W. R. Kirner, *J. Amer. Chem. Soc.*, **50**, 1955 (1928); T. Reichstein, *Ber.*, **63**, 751 (1930); O. Moldenhauer, *Ann. Chem.*, **580**, 180 (1953).

(20) Utilization of *t*-butylamine was necessitated by the discovery that the conventional reagent for this purpose, *n*-butylamine, gave products from displacement on **1** in addition to the desired conversion of **2**.

(21) A. Jurasek and J. Kovac, *Chem. Zvesti*, **19**, 840 (1965); *Chem. Abstr.*, **64**, 5027*e* (1966).

(22) The equilibrium concentrations starting from pure **1** and **2** were established at 81, 101, 120, and 141° in acetonitrile, 81° in sulfolane and dimethylformamide, and 150° for all other solvents.

(23) Benzyl thiocyanate (**5**) was obtained from Aldrich Chemical Co.