The Nature of the Carbonium Ion. VIII. Cycloalkyl Cations from Thiocyanate Isomerizations

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Thermal isomerizations of cyclopropylcarbinyl (**1**), cyclobutyl (**2**), cyclopentyl (**4**), and cyclooctyl (**5**) thiocyanates were effected in sulfolane and, where appropriate, less polar aprotic solvents. In these cases, formation of isomeric isothiocyanates at relative rates which paralleled the relative rate order observed for acetolyses of the corresponding *p*-toluenesulfonate esters indicated the intermediacy of cycloalkyl cations. The cyclobutyl related compounds, **1** and **2**, isomerized to similar product mixtures but at vastly different rates. The product ratios observed in these cases did not resemble those from solvolyses of the analogous arylsulfonate esters, thereby suggesting that the partition of the intermediate ion(s) is governed largely by the proximity of the counterion in the intermediate ion pairs. Studies of the isomerizations of **1** with ionic and Lewis acid catalysts supported this notion. The larger cycloalkyl thiocyanates **4** and **5** isomerized only to their corresponding skeletally unrearranged isothiocyanate isomers **9** and **10**, respectively. Reaction rates were in keeping with the relative driving forces to ionization for these secondary thiocyanates. Interpretations of the results are presented involving ion pair intermediates in which counterion position is largely influential in determining product compositions.

We have previously utilized the thiocyanate isomerization technique for examination of ion pairs[3] to study cationic intermediates which were generated by π participation and σ participation in bridged bicyclic systems.[4] In this paper we described the application of the technique to monocyclic cations. From the earlier work it was apparent that, among the nonallylic representatives of this category, only a few would be appropriate for study. The reason for the restriction lies primarily in the relative sluggishness of the reaction which only allows isomerizations, at detectable rates, for those primary and secondary thiocyanates which receive appreciable intramolecular assistance in ionization. Since we had established in the previous paper of this series[4e] a fair correlation between the rates of thiocyanate isomerization and the rates of acetolysis of the corresponding *p*-toluenesulfonate esters, we felt that the cyclobutyl (and its related cyclopropylcarbinyl), cyclopentyl, and cyclooctyl thiocyanates should be representative types which would isomerize and provide us with meaningful information. (Cyclohexyl thiocyanate had already been shown by us to be thermally unisomerizable[4c]).

Interest in the cyclobutyl–cyclopropylcarbinyl system stems from a prior examination[5] of the isomerization, in dimethylformamide, of cyclopropylcarbinyl thiocyanate (**1**). As subsequent work has shown that dimethylformamide induces anomalous results for other thiocyanates,[4b] it was of importance for comparison's sake to thoroughly study the isomerization of **1** in the better ionizing, less nucleophilic solvent, sulfolane. It was also considered likely that cyclobutyl thiocyanate (**2**), which was inert in dimethylformamide, would isomerize in sulfolane to provide more information on the role of the counterion in the skeletal partition of the intermediate cation(s). Cyclopentyl and cyclooctyl thiocyanates were interesting, in that their driving forces to ionization (if indeed they *did* isomerize) were only torsional and "I" strain—two factors which had not previously been demonstrated as sufficient to cause isomerization.

We therefore prepared these four thiocyanates, as well as allylcarbinyl thiocyanate (**3**), which is related to the cyclobutyl–cyclopropylcarbinyl series, along with their corresponding isothiocyanates, and subjected them to thermal isomerization conditions.

Results

Cyclopropylcarbinyl thiocyanate (**1**) was prepared from the corresponding *p*-toluenesulfonate[6] by displacement with potassium thiocyanate in anhydrous acetone. This method afforded material in excess of 98% purity. Further purification was effected by reaction of the isothiocyanate impurities with *n*-butylamine followed by preparative gc separation of the remaining thiocyanates. Pure **1** exhibited the characteristic organic thiocyanate infrared absorption at 2160 cm^{-1} (strong, sharp).

Allylcarbinyl thiocyanate (**3**) was synthesized by the same procedure used for **1**. Allylcarbinyl *p*-toluenesulfonate[7] was treated with potassium thiocyanate in anhydrous acetone. Material prepared in this fashion had a small isothiocyanate impurity (~10% by infrared) which was removed, as before, by treatment with *n*-butylamine.

As no direct displacement route could be found to afford cyclobutyl thiocyanate (**2**) free of other skeletal isomers,[8] a more elaborate route was employed. Cyclopropylcarbinyl thiocyanate (**1**) was isomerized for approximately 10 hr at reflux in 0.15 *M* benzene solution containing 2% (w/v) of boron trifluoride etherate.

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(2) From the thesis submitted by R. K. Porter in fulfillment of the requirements for the M.S. degree, Temple University, 1970.

(3) For recent reviews see (a) L. A. Spurlock and T. E. Parks in "Mechanisms of Reactions of Sulfur Compounds," Vol. 3, N. Kharasch, Ed., Intra-Science Research Foundation, Santa Monica, Calif., 1970 p 161; (b) A. Fava in "Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Permagon Press, Oxford, 1966, p 85. See also (c) A. Fava, *et al.*, *J. Amer. Chem. Soc.*, **87**, 1045 (1965); (d) A. Ceccon, A. Fava, and I. Papa, *Chim. Ind. (Milan)*, **51**, 53 (1969), and references cited therein.

(4) (a) L. A. Spurlock and W. G. Cox, *J. Amer. Chem. Soc.*, **91**, 2961 (1969); (b) L. A. Spurlock and R. G. Fayter, *J. Org. Chem.*, **34**, 4035 (1969); (c) L. A. Spurlock and T. E. Parks, *J. Amer. Chem. Soc.*, **92**, 1279 (1970); (d) L. A. Spurlock and R. J. Schultz, *ibid.*, **92**, 6302 (1970); (e) L. A. Spurlock and W. G. Cox, *ibid.*, **93**, 146 (1971); (f) L. A. Spurlock and Y. Mikuriya, *J. Org. Chem.*, **36**, 1549 (1971).

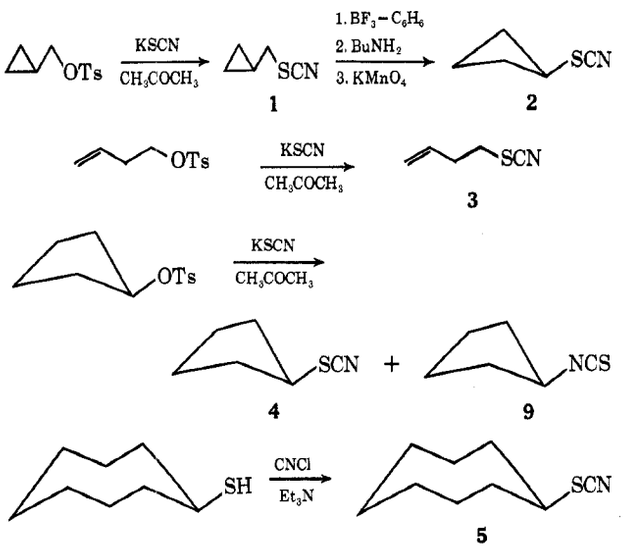
(5) L. A. Spurlock and P. E. Newallis, *Tetrahedron Lett.*, **No. 3**, 303 (1966).

(6) G. G. Bergstrom and S. Siegel, *J. Amer. Chem. Soc.*, **74**, 145 (1952).

(7) K. L. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964).

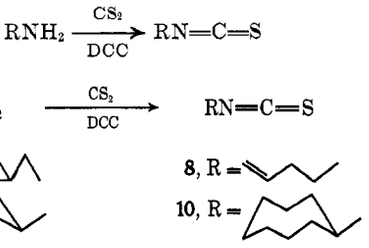
(8) Attempted displacements with thiocyanate ion on cyclobutyl chloride, bromide, or *p*-toluenesulfonate yielded only intractable mixtures.

The extent of isomerization was monitored by gc. When the concentration of **2** in the mixture seemed to be at a maximum, the mixture was worked up and then treated with *n*-butylamine to remove isothiocyanates. The resulting mixture of thiocyanates **2**, **1**, and **3** was then treated with saturated aqueous potassium permanganate at room temperature to remove thiocyanates **1** and **3**. Distillation afforded yet another mixture consisting mainly of **2** with a small amount of **1** remaining. Pure **2** was obtained from this mixture by preparative gc.



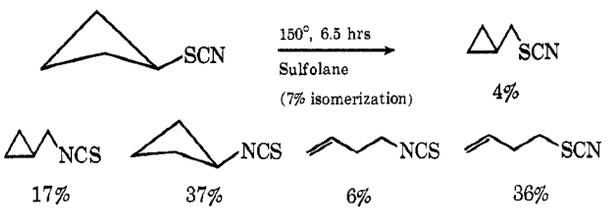
The potassium thiocyanate displacement of cyclopentyl *p*-toluenesulfonate afforded cyclopentyl thiocyanate (**4**) and the corresponding isothiocyanate (**9**). The two compounds were separated by chromatography on silica gel. Cyclooctyl thiocyanate (**5**), being inaccessible by the displacement route (much decomposition of the reactive *p*-bromobenzenesulfonate occurred), was obtained from cyanogen chloride treatment of cyclooctylthiol[9] in ether and triethylamine solution. Thiocyanate obtained in this fashion was utterly free of isothiocyanates.

Allylcarbinyl isothiocyanate (**8**) was obtained by treatment of the corresponding amine[10] with *N*,*N*′-dicyclohexylcarbodiimide[11] and carbon disulfide in ether at 10°. By the same procedure used for **8**, cyclobutyl isothiocyanate (**7**), cyclopropylcarbinyl isothiocyanate (**6**), and cyclooctyl isothiocyanate (**10**) were prepared from cyclobutylamine,[12] cyclopropylcarbinylamine,[10] and cyclooctylamine, respectively. Purifications were accomplished by distillation followed by preparative gc. Isothiocyanates **6**–**10** all exhibited typical organic isothiocyanate infrared absorptions at 2200–2000 cm^{-1} (strong, broad) as characteristic doublets. The *N*-phenylthiourea derivatives used to characterize **6**, **7**, and **8** were all prepared by treating the appropriate isothiocyanate with freshly purified aniline without solvent, followed by recrystallization of the crude material from ether–pentane.



The infrared and nmr spectra for all compounds were in accord with the structural assignments, and minimum purity in excess of 99.5% could be confirmed by gc and elemental analyses. All product and kinetic studies were conducted by gc, with structural assignments being made on the basis of comparison of retention times with those of authentic samples on two different columns.

In the cyclobutyl–cyclopropylcarbinyl series, control experiments confirmed the expectation that isothiocyanates **6**, **7**, and **8** and thiocyanate **3** were stable under the reaction conditions employed.[13] Thiocyanate **2** did, however, exhibit isomerization to the extent of 7% in sulfolane at 150° after 6.5 hr. The following product distribution (in relative per cent) was observed.



The slow isomerization rate and decomposition of some of the products on prolonged heating negated attempts to obtain accurate rate data. It was clear, however, that a large enough difference existed between the isomerization rates of cyclobutyl and cyclopropylcarbinyl thiocyanates that product distributions from the latter would not be markedly affected by secondary isomerizations of **2**.[14]

A more thorough examination of isomerizations of **1** was thus undertaken. Table I summarizes the results of solvent and temperature influences on the relative product ratios and relative isomerization rates of 0.150 *M* solutions of **1**. Values listed are the averages of at least two runs with overall material balances in excess of 90%.

The effects of varying the concentration of **1** were studied over a 100-fold range (0.015 *M* to 1.50 *M*). Results are seen in Table I. The decrease in extent of isomerization with increasing initial concentration of **1** is most readily explained as being caused by a decrease in the ionizing power of the isomerizing medium upon dilution with nonpolar **1**. This observation suggested that any bimolecular route to isomerization was improbable.

(9) (a) R. Frank and P. V. Smith, *J. Amer. Chem. Soc.*, **68**, 2103 (1946); (b) Sandler and Karo, "Organic Functional Group Preparations," Academic Press, New York, N. Y., 1968, p 483.

(10) J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.*, **73**, 2509 (1951).

(11) J. C. Jochims and A. Seeliger, *Angew. Chem., Int. Ed. Engl.*, **6**, 174 (1967).

(12) J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3413 (1966).

(13) Cyclopropylcarbinyl isothiocyanate (**6**) could be forced to isomerize to the extent of ~10% after 92 hr in sulfolane at 150°. The product mixture consisted of all thiocyanates and isothiocyanates of this series (**1**–**3**, **7**, and **8**). Because of its slowness, the reaction could have no influence on isomerizations of **1**, and is of interest only in that it is one of the few observed "reverse" thermal isomerizations.

(14) The subsequent observation that product distributions from **2** and **1** were quite similar reinforces this assumption.

TABLE I

ISOMERIZATIONS OF 0.150 *M* SOLUTIONS OF CYCLOPROPYLCARBINYL THIOCYANATE

Solvent	Temp, °C	Time, hr	% isomerization	Relative product, %
CH_3CN	130	12	2.8	6 22 38 11 22
		48	9.6	6 21 37 13 23
	140	6	2.8	5 22 42 10 22
		12	6.2	5 20 39 13 23
		24	11.9	5 20 39 13 23
	150	6	9.1	6 22 38 12 21
		12	14.3	6 21 39 13 21
Sulfolane	130	12	18.8	6 22 36 14 23
		48	55.0	6 22 35 15 22
	140	6	22.4	6 20 36 14 22
		12	40.2	6 20 37 15 22
		24	62.8	6 21 36 16 22
	150	6	46.3	6 21 36 15 20
		6[a]	48	6 22 37 14 21
		6[b]	36	6 20 39 16 20
		12	69.6	6 20 36 16 20
DMA[c]	150	6	23.0	5 10 39 34 11
DMF[d]	150	6	40.0	5 9 34 38 15

[a] 0.015 *M* solution. [b] 1.500 *M* solution. [c] Dimethylacetamide. [d] Dimethylformamide.

TABLE II

CATALYZED ISOMERIZATIONS OF 0.150 *M* SOLUTIONS OF CYCLOPROPYLCARBINYL THIOCYANATE IN SULFOLANE AT 150.0°

Catalyst	Concn, *M*	Time, hr	% isomerization	Relative product, %[a]
$KClO_4$	0.010	6	46.8	7 20 36 16 20
	0.100	6	55.5	7 20 34 18 22
KSCN	0.010	6	54.4	6 18 45 14 18
	0.100	6	79.2	4 10 68 8 10
$BF_3 \cdot Et_2O$[b]	2% (w/v)	2	20.5	5 13 23 18 42
		6	47.3	3 9 17 21 50
		10	68.0	3 8 14 22 54

[a] Values are averages of two runs. [b] In benzene at 80°.

Effects of catalysts were also studied using potassium perchlorate, potassium thiocyanate, and boron trifluoride as the catalytic substances. Table II lists these product distributions.

Isomerization rates were followed by gc. Specific rate constants were determined graphically by measuring the slopes of plots of log [RSCN] *vs.* time. Rate data obtained in this fashion are listed in Table III. Linear plots were obtained for all solvents studied. As expected, the isomerization was found to be more efficient in the more polar solvent, sulfolane, than in acetonitrile. The catalyzed isomerizations were also found to be first-order processes, although rate plots for the 0.100 *M* thiocyanate catalyzed runs began to deviate slightly from linearity. The effect of boron trifluoride catalysis is perhaps the most striking of these results in light of the fact that **1**, in benzene alone, would not isomerize even at 150°.

Cyclopentyl thiocyanate (**4**) and cyclooctyl thiocyanate (**5**) were subjected to product studies analogous to those applied to **1**. In both cases only the skeletally unrearranged isothiocyanate (**9** and **10**, respectively) was obtained. The rate of isomerization for **4**, being quite slow (1.86×10^{-6} sec^{-1}), was measured only in sulfolane at 150°. The cyclooctyl compound, however, isomerized at a comparatively rapid rate, and so rate measurements were conducted in acetonitrile as well as sulfolane and at two temperatures. The rates in these solvents were as follows: sulfolane, 3.0×10^{-5} sec^{-1} ($t_{1/2}$ = 6.5 hr) at 150°; 2.5×10^{-6} sec^{-1} ($t_{1/2}$ = 78 hr) at 130°; and acetonitrile, 3.6×10^{-6} sec^{-1} ($t_{1/2}$ = 54 hr) at 150°.

Discussion

The rate data from **1**, and particularly the strong dependence on solvent ionizing power, indicate a rate-determining step consisting of the unimolecular dissociation of a neutral molecule into ions. As expected for such a process, product ratios were found to be essentially independent of time, temperature, and changes in the concentration of **1** over a wide range. By analogy to other alkyl thiocyanate isomerizations,[3b,4] the ionization is thought to proceed very little past the intimate ion pair stage. Although no experiments were carried out to determine the extent of further dissociation to solvent-separated or "free" ion pairs, it seems reasonable to assume a limit of *ca.* 10–12% for this process.[15] The invariance of product ratios with temperature and time confirms that no significant secondary processes are occurring; thus the products observed may be con-

(15) This is based on a similar limit, determined by isotopic labeling experiments, for isomerizations of *exo*-2-norbornyl thiocyanate.[4c] As the isomerization rates of this compound and **1** are quite close, it is reasonable to assume that they will possess approximately the same dissociative properties.

TABLE III

ISOMERIZATION RATES OF 0.150 *M* SOLUTIONS OF CYCLOPROPYLCARBINYL THIOCYANATE

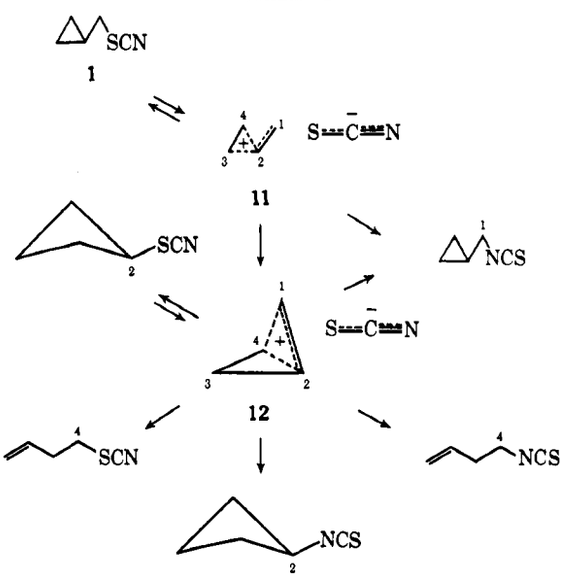
Solvent	Temp, °C	Catalyst	Concn, *M*	$k \times 10^6$ sec^{-1}	$t_{1/2}$, hr
CH_3CN	130			0.578 ± 0.021	333.7
	140			1.46 ± 0.03	131.8
	150			3.66 ± 0.15	52.6
Sulfolane	130			4.49 ± 0.13	43.0
	140			11.2 ± 0.2	17.0
	150			27.0 ± 0.4	7.12
	150	$KClO_4$	0.010	29.4 ± 0.6	6.56
	150	$KClO_4$	0.100	34.9 ± 0.4	5.52
	150	KSCN	0.010	32.2 ± 0.9	5.99
	150	KSCN	0.100	57.7 ± 2.9	3.34
Benzene	80	$BF_3 \cdot Et_2O$	2% (w/v)	30.7 ± 0.3	6.27
CH_3CN: $\Delta H^{\ddagger} = 31$ kcal/mol				$\Delta S^{\ddagger}_{130°} = -10$ eu	
Sulfolane: $\Delta H^{\ddagger} = 30$ kcal/mol				$\Delta S^{\ddagger}_{130°} = -8$ eu	

sidered as mainly the results of the partition of the initial intimate ion pairs.

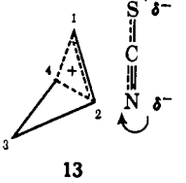
Since the isomerization of **1** proceeds much more rapidly than that of most primary thiocyanates, there is indication that anchimeric assistance to ionization is taking place, as was observed[16] in other carbonium ion reactions of cyclopropylcarbinyl derivatives. This effect is thought to be due to a release of strain in the cyclopropyl ring[16e] and, to a lesser extent, to stabilization of the incipient carbonium ion by delocalization of charge into the ring.[16c] The similarity of the activation parameters calculated for the thiocyanate isomerization with those found by Roberts[17] for homoallylically assisted solvolyses would seem to support the idea of assisted ionization for **1**. If one assumed that the initial carbonium ion formed, **11**, is similar to the cyclopropylcarbinyl ion of the transition state, further rearrangement is necessary to provide the intermediate ion (**12**) from which products of different structure are derived. In the mechanistic picture presented in Scheme I, this second intermediate is represented as the unsymmetrical bicyclobutonium ion (**12**).[18] Alternatively, a set of ions centered about the "symmetrical bicyclobutonium" ion could be postulated.[16b] We have chosen to represent the product-forming ion as **12** mainly for the sake of simplicity, and because our results do not allow us to distinguish between the two types of ions.[19]

For these reactions product formation represents a competition between the S and N ends of the thiocyanate anion for capture of the electrophilic sites of the cations. In carbonium ion reactions, the S end of the thiocyanate anion has been reported to be more nucleophilic than the N end by a factor of about 2–9.[3b,4c] The data outlined in Table I show an average S/N

SCHEME I



ratio of 0.6 for all the products, *i.e.*, (**2**, **3**)/(**6**, **7**, **8**). Isothiocyanate **6** however, can arise by N capture of the first-formed, cyclopropylcarbinyl intermediate, **11** (S capture regenerates starting material), as well as through attack on **12**. The S/N ratio for *all* the products is thus misleading. Comparison of the *rearranged* product ratios reveals S/N ratios of 2.3 for the allylcarbinyl products (**3**/**8**) and 1.0 for cyclobutyl products (**2**/**7**). The latter "abnormally" low S/N ratio shows some unusual preference for N-end attack by the thiocyanate anion on C_2 of the bicyclobutonium ion. Clearly, in the early stages of its formation, ion **12** still retains the majority of positive charge at C_1, which is partially "solvated" by the S end of the leaving group. Attack by the N end of thiocyanate could occur at C_2 *via* a semicyclic mechanism as illustrated in **13**. A similar mechanism could be envisioned as increasing N attack at C_4; however, the longer C_1–C_4 bond length



13

(16) (a) K. B. Wiberg and J. G. Pfeiffer, *J. Amer. Chem. Soc.*, **92**, 553 (1970); (b) K. B. Wiberg and G. Szeimes, *ibid.*, **92**, 571 (1970); (c) P. v. R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2322 (1968); (d) R. Breslow in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 259–280; (e) S. Winstein and E. M. Kosower, *J. Amer. Chem. Soc.*, **81**, 4397 (1959).

(17) (a) D. D. Roberts, *J. Org. Chem.*, **34**, 285 (1969); (b) D. D. Roberts and T. M. Watson, *ibid.*, **35**, 978 (1970).

(18) A more accurate representation might include an equilibrating set of bicyclobutonium ions; however, only one is used here for the sake of simplicity.

(19) By analysis of the preliminary results reported by Spurlock and Newallis[5] on the isomerization of **1**, Majerski, *et al.* [see *Tetrahedron*, **23**, 661 (1967)] also deduced that the intermediate must be a bicyclobutonium ion. Careful consideration of the factors involved in their arguments leads one to question the certainty of this conclusion. The bicyclobutonium ion was nevertheless adopted as the best representation of the second product-forming intermediate for clarity of presentation.

in the early phase of bicyclobutonium ion formation may preclude this. An alternative explanation might simply reside in different relative electronic requirements for S-end and N-end attacks at C_2 and C_4, since it is conceivable that in the initial stages of the formation of **12** more charge would reside on C_2 than on C_4.

The slight trends in product ratios observed with increasing ionizing strength of the solvent (perchlorate ion catalysis) are best explained in terms of greater ionic mobility. The small decrease in proportion of **6** is probably due to a less efficient capture of the first formed intermediate **11** as solvation of the ion pair is improved. The increases in allylcarbinyl products **3** and **8** may be related to an increased lifetime of the bicyclobutonium ion pair, allowing for more efficient migration by the thiocyanate anion to C_4. The failure of thiocyanate ion catalysis to show similar trends (in that a substantially increased percentage of isothiocyanate **6** was observed) indicates only that a bimolecular displacement process is occurring in competition with unimolecular dissociation.

Catalysis by boron trifluoride ethereate in benzene solution illustrates yet another mode for isomerization. In this case, the effectiveness of the catalyst leads toward an equilibration of the thiocyanate ring skeleta. This is best seen through the time dependence of the product ratios (Table II). Additional experiments at longer reaction times showed a decrease in the relative amount of cyclobutyl thiocyanate (**2**) after reaching a maximum proportion, accompanied by an increase in proportion of the inert allylcarbinyl thiocyanate (**3**). No attempt was made to follow the reaction to completion owing to the slowness of the conversion **2** → **3**, but an analogous situation has been described by Olah and Lin[20] in the aluminum chloride catalyzed isomerizations of cyclopropylcarbinyl chloride, first to cyclobutyl chloride and then to allylcarbinyl chloride. The fact that, in this case, thiocyanate products were formed preferentially to isothiocyanates has been attributed to the ability of the Lewis acid to coordinate with the N end of the thiocyanate moiety, thereby suppressing N-bound product formation. One may therefore suppose that the ultimate composition under these conditions would consist mainly of thiocyanate **3** with small amounts of isothiocyanates **6**, **7**, and **8**.

Isomerizations of **1** in the more nucleophilic solvents, dimethylformamide and dimethylacetamide, also produced a marked enhancement of the relative per cent of thiocyanate **3** in the products. This effect is thought to be due to ionization processes which are assisted by these nucleophilic solvents,[4b] resulting in loosely bound solvent–carbonium ion complexes. If this is the case, the more nucleophilic S end of the thiocyanate moiety might be expected to be more efficient in liberating the carbonium ions from the complexes, leading to increased thiocyanate products.

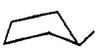
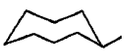
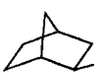
In general, the thermal isomerizations of **1** seem well characterized as anchimerically assisted, unimolecular dissociation processes, in which ion pairs and counterion mobility play important roles in structural partition. In all likelihood the isomerization of cyclobutyl thiocyanate (**2**) may be described in the same fashion.

By contrast, the less complicated isomerizations of cyclopentyl (**4**) and cyclooctyl (**5**) thiocyanates are clearly dissociation–recombination reactions in which structural features allow for no skeletal modifications[21] during the ion pair phase. The unusual feature of these reactions lies in the fact that they are the first observations of uncatalyzed[22] secondary thiocyanate isomerization occurring with no neighboring group assistance. It is usually assumed that torsional strain exerts a driving force to ionization of cyclopentyl and cyclooctyl derivatives, and this would seem to be the reason for the isomerizations of **4** and **5**. The previously mentioned failure of the unstrained cyclohexyl thiocyanate to isomerize adds support to this explanation.

The relationship between rates of thiocyanate isomerizations in sulfolane and rates of acetolysis by the corresponding *p*-toluenesulfonates again essentially holds. (See Table IV and ref 4e.) Based on these facts we now feel secure in the ability to predict the probability of obtaining a thermal thiocyanate–isothiocyanate interconversion, and to suggest likely rates of transformation.

TABLE IV

COMPARISON OF RELATIVE THIOCYANATE ISOMERIZATION RATES IN SULFOLANE WITH *p*-TOLUENESULFONATE ACETOLYSIS RATES

Alkyl group	RSCN rel rate 150°	ROTs rel rate 25°
	1.14	26.7
	0.04	0.20
	0.08	0.19
	1.3	3.4
	1	1

Experimental Section[23]

Cyclopropylcarbinyl Thiocyanate (1).—To a mechanically stirred solution of 33.0 g (0.340 mol) of potassium thiocyanate in 1.3 l. of anhydrous acetone was added rapidly 74.2 g (0.327 mol) of crude cyclopropylcarbinyl *p*-toluenesulfonate[8] in 100 ml of acetone. Precipitation began before the addition was complete (10 min). The resulting mixture was allowed to stir overnight at room temperature. The precipitated salt was removed by filtration and washed well with pentane. The acetone filtrate

(20) G. A. Olah and C.-H. Lin, *J. Amer. Chem. Soc.*, **90**, 6468 (1968).

(21) It is conceivable that some hydride shifts could occur during these isomerizations, thereby changing the carbon of attachment for the functional group. We consider this possibility unlikely, or at best affording a minimal contribution to the reaction, since the ordinarily facile 2,6-hydride shifts of the 2-norbornyl cation were shown[4c] to be completely suppressed during isomerizations of *exo*-2-norbornyl thiocyanate.

(22) *sec*-Butyl thiocyanate can be isomerized, albeit slowly, when boiled with zinc chloride. See P. A. S. Smith and D. W. Emerson, *J. Amer. Chem. Soc.*, **82**, 3076 (1960).

(23) Melting and boiling points were uncorrected. Infrared spectra were obtained on a Perkin-Elmer Infracord Model 137B using sodium chloride optics. A Perkin-Elmer Model F-11 gas chromatograph was employed for analyses of isomerization mixtures and kinetics, using two columns: a 6 ft × 1/8 in. 30% phenyl diethanolamine succinate (PDEAS) on 60/80 mesh Chromosorb W, and a 6 ft × 1/8 in. 20% diethylene glycol succinate (LAC-728) on 60/80 mesh Chromosorb W. Elemental anslyses were performed by Micro-Analysis, Inc., of Wilmington, Del. Organic solvents were of A. C. S. reagent grade unless otherwise specified. Dioxane was purified by the method described by Fieser. [See "Experiments in Organic Chemistry," third ed.] Sulfolane was distilled from potassium permanganate under vacuum. Dimethylformamide was distilled from calcium hydride. Aniline was purified by distillation from zinc dust.

was divided into two portions, both of which were worked up by addition of 1.0 l. of water and extracted several times with pentane. The combined pentane solutions were washed with water and dried over magnesium sulfate. Evaporation of the solvent and vacuum distillation of the crude product gave 14.7 g (40%) of **1**, bp 73.5–76.5° (10 mm) [lit.[5] bp 76.3–77.2° (14 mm)]. This was shown by gc to be 98% pure. The small isothiocyante impurity was removed by treating the product with 3 ml of *n*-butylamine in the absence of solvent for 0.5 hr. Pentane (50 ml) was added and the solution was washed twice with 10% hydrochloric acid, dried over magnesium sulfate, and concentrated. Distillation gave 10.6 g of pure **1**, bp 75.8–76.0° (10 mm).

A completely homogeneous sample of **1** was also obtained by preparative gc (6 ft × 0.5 in. LAC-728 column) and had ir (film) 3000, 2160, 1425, 1255, 1025, 970, 920, and 835 cm^{-1}; nmr (CCl_4) τ 7.05 (d), 8.60–9.02 (m), 9.02–9.78 (m).

Anal. Calcd for C_5H_7NS: C, 53.06; H, 6.23; N, 12.38. Found: C, 53.36; H, 6.23; N, 12.24.

Cyclobutyl Thiocyanate (2).—To a magnetically stirred solution of 3.52 g (0.0248 mol) of boron trifluoride etherate in 170 ml of benzene being heated at reflux was added in one portion a solution of 3.00 g (0.0265 mol) of **1** in 6 ml of benzene. The course of the reaction was followed by gc. After 10 hr, when the concentration of **2** seemed to be at a maximum, the reaction was quenched by pouring into 100 ml of saturated sodium bicarbonate solution. The organic layer was separated and the aqueous solution was extracted with 50 ml of pentane. The combined organic extracts were washed with water and dried over magnesium sulfate. Removal of the solvent under vacuum left 2.85 g of an orange liquid shown by gc to consist of a complex mixture, 37% of which was the desired **2**. The isothiocyanate impurities were removed by treating the mixture with 3 ml of *n*-butylamine in the absence of solvent for 1 hr. Pentane (50 ml) was added and the solution was washed twice with 10% hydrochloric acid, dried over magnesium sulfate, and concentrated. The yellow residue, amounting to 1.86 g, was then dissolved in 50 ml of pentane and treated with 50 ml of a saturated aqueous potassium permanganate solution. After stirring at room temperature for 0.5 hr, the organic layer was separated and the aqueous layer was extracted twice with 25 ml of pentane. The combined pentane solutions were washed with water and dried over magnesium sulfate. Removal of the solvent under vacuum left 1.17 g of a yellow liquid. This mixture was flash distilled at 10 mm, affording a mixture consisting of 88% of **2**. Pure **2** was collected from the mixture by preparative gc on a 7 ft × 3/8 in. 25% PDEAS column. This material had bp 69.0–70.0° (10 mm); ir (film) 3000, 2950, 2150, 1440, 1280, 1010, 820, and 720 cm^{-1}; nmr ($CDCl_3$) τ 6.20 (quintet), 7.25–8.50 (m).

Anal. Calcd for C_5H_7NS: C, 53.06; H, 6.23; N, 12.38. Found: C, 53.30; H, 6.28; N, 12.46.

Allylcarbinyl Thiocyanate (3).—To a mechanically stirred solution of 5.04 g (0.052 mol) of potassium thiocyanate in 75 ml of anhydrous acetone was added dropwise 11.62 g (0.051 mol) of crude allylcarbinyl *p*-toluenesulfonate[7] in 25 ml of acetone. The mixture was heated at reflux for 66 hr. Upon cooling, the mixture was filtered with suction and the precipitated solid was washed well with acetone. The combined filtrate and washings were concentrated under vacuum to a semisolid residue which was triturated with pentane. Vacuum evaporation of this solvent left 5.62 g (97%) of crude **3**, estimated to have 10% isothiocyanate impurity by infrared analysis. The crude product was purified by treatment with 1.82 g (0.025 mol) of *n*-butylamine in 60 ml of anhydrous dioxane. After stirring for 17 hr at room temperature, the reaction mixture was poured into 350 ml of water and extracted with pentane. The combined extracts were washed with 10% hydrochloric acid followed by saturated sodium bicarbonate solution and dried over magnesium sulfate. Evaporation of the solvent followed by distillation of the residue gave 3.30 g (57%) of pure **3**, bp 65–77° (11.5 mm) [lit.[5] bp 75.5–76.2° (18 mm)]. A completely homogeneous sample of **3** obtained by preparative gc (6 ft × 3/8 in. LAC-728 column) had bp 65.0–67.0° (9.5 mm); ir (film) 2900, 2170, 1650, 1440, 1285, 1000, and 930 cm^{-1}; nmr (CCl_4) τ 3.86–4.58 (m), 4.65–5.08 (m), 7.02 (t), 7.49 (q).

Anal. Calcd for C_5H_7NS: C, 53.06; 6.23; N, 12.38. Found: C, 53.08; H, 6.07; N, 12.63.

Cyclopentyl Thiocyanate (4) and Isothiocyanate (9).—To a mechanically stirred solution of 10.67 g (0.110 mol) of potassium thiocyanate in 500 ml of anhydrous acetone was added in one portion a solution of 23.8 g (0.099 mol) of crude cyclopentyl *p*-toluenesulfonate[24] in 50 ml of acetone. The solution was heated at reflux overnight. The reaction mixture was concentrated under vacuum and the resulting residue was triturated with pentane. The pentane solution was washed with water, dried, and concentrated to yield 11.30 g (90%) of a gold liquid shown by gc to consist of 75% **4** and 25% **9**. Chromatography on silica gel (300 g) gave a complete separation of these materials, with **9** being eluted first by pentane and **4** ultimately eluted with ether.

Thiocyanate **4** was obtained in the amount of 7.24 g after distillation: bp 87.0° (10 mm); ir (film) 2960, 2870, 2150, 1450, 1440, 1320, 1240, 1020, 930, 890, and 805 cm^{-1}; nmr ($CDCl_3$) τ 6.25–6.60 (m), 7.59–8.60 (m); mass spectrum (50 eV) *m/e* 127 (12), 69 (90), 68 (25), 67 (32), 41 (100), and 39 (31).

Isothiocyanate **9** was obtained in the amount of 1.40 g after distillation: bp 80.0° (10 mm); ir (film) 2960, 2870, 2200–2000, 1450, 1440, 1350, 1340, 1315, 1280, 1070, 935, 880, and 800 cm^{-1}; nmr ($CDCl_3$) τ 5.70–6.12 (m), 7.80–8.70 (m); mass spectrum (50 eV) *m/e* 127 (70), 69 (100), 68 (67), 67 (35), 41 (37), and 39 (39).

Cyclooctyl Thiocyanate (5).—A solution of 40.2 g (0.28 mol) of cyclooctylthiol[9] and 34.87 g (0.34 mol) of triethylamine in 100 ml of dry ether was added dropwise to a solution of 17.7 g (0.34 mol) of cyanogen chloride in 200 ml of dry ether. The bath temperature was maintained below −15° during the addition and then allowed to slowly come to room temperature overnight. The white solid which had formed was filtered off and washed several times with ether. The filtrate and washings were combined and washed three times with 100 ml of water, three times with 50 ml of saturated sodium bicarbonate solution, two times with 50 ml of 10% hydrochloric acid, and finally three more times with 100 ml of water. The ether layer was dried and concentrated, affording 51.0 g of a dark brown liquid. The crude material was distilled at 60–64° (0.07 mm) yielding 22.8 g (48.3%) of a colorless liquid. Gc analysis proved this to be an approximately equal mixture of two compounds, one of which could be identified as the desired thiocyanate, **5**. Separation of pure **5** was accomplished by distillation on a 24-in. Teflon spinning band column: bp 61–64° (0.07 mm); mass spectrum (50 eV) *m/e* 169 (1.9), 111 (10.5), 110 (15.2), 82 (40), 81 (37), 69 (41), 68 (44), 67 (48), 57 (100), and 55 (43).

Cyclopropylcarbinyl Isothiocyanate (6).—As in the procedure described for **8**, 2.12 g (0.03 mol) of cyclopropylcarbinyl amine in 1 ml of ether was treated with 6.18 g (0.03 mol) of *N,N*-dicyclohexylcarbodiimide and 18 ml (22.7 g, 0.30 mol) of carbon disulfide in 50 ml of ether to yield, after distillation, 2.20 g (65%) of **6**, bp 81.5–82.5° (21 mm) [lit.[5] bp 78.0–79.0° (20 mm)]. A completely homogeneous sample of **6**, obtained by preparative gc (6 ft × 0.5 in. LAC-728 column), had bp 65° (10 mm); ir (film) 2220, 2000, 1440, 1380, 1320, 1020, 990, 930, and 835 cm^{-1}; nmr ($CDCl_3$) τ 6.58 (d), 8.40–9.02 (m), 9.04–9.88 (m).

Anal. Calcd for C_5H_7NS: C, 53.06; H, 6.23; N, 12.38. Found: C, 53.21; H, 5.98; N, 12.16.

1-Cyclopropylcarbinyl-3-phenylthiourea.—A magnetically stirred mixture of 1.00 g (8.85 mmol) of **6** and 1.00 g (10.8 mmol) of aniline was allowed to stir overnight at room temperature, then cooled to induce crystallization. The resulting solid was pulverized, triturated with pentane, and air dried to yield the crude thiourea in the amount of 1.83 g (100%). Two recrystallizations from 50% ether–pentane gave a sample: mp 94.0–94.6°; ir (Nujol) 3300, 3130, 1590, 1540, 1510, 1310, 1230, 1140, 920, 790, 730, and 680 cm^{-1}; nmr ($CDCl_3$) τ 2.50–3.08 (m), 3.74 (br s), 6.58 (d d), 8.64–9.32 (m), 9.34–9.90 (m).

Anal. Calcd for $C_{11}H_{14}N_2S$: C, 64.04; H, 6.84; N, 13.58. Found: C, 63.80; H, 6.90; N, 13.66.

Cyclobutyl Isothiocyanate (7).—Cyclobutyl isothiocyanate was prepared by the procedure used for **8** with minor changes (the ethereal amine solution was added in one portion and the reaction time was shortened to 18 hr). In this preparation, 5.33 g (0.075 mol) of cyclobutylamine[12] in 20 ml of ether was treated with 15.42 g (0.075 mol) of *N,N'*-dicyclohexylcarbodiimide and 45 ml (57 g, 0.75 mol) of carbon disulfide in 150 ml of ether to yield, after distillation, 7.02 g (82%) of **7**: bp 65.5–66.0° (10.5 mm) [lit.[5] bp 77.4–78.5° (28 mm)]; ir (film) 3000, 2280–2000, 1340, 1140, 1030, 980, 940, 810, and 708 cm^{-1}; nmr (CCl_4) 5.90 (quintet), 7.30–8.50 (m).

Anal. Calcd for C_5H_7NS: C, 53.06; H, 6.23; N, 12.38. Found: C, 53.06; H, 6.43; N, 12.34.

(24) J. D. Roberts and V. C. Chambers, *J. Amer. Chem. Soc.*, **73**, 5034 (1951).

1-Cyclobutyl-3-phenylthiourea.—A mixture of 1.00 g (8.85 mmol) of **7** and 0.830 g (8.93 mmol) of aniline was allowed to stir overnight at room temperature. The solidified reaction mixture was pulverized and recrystallized from ether, yielding 1.66 g (91%) of the desired thiourea as fine needles: mp 100.5–101.5°; ir (Nujol) 3300, 3210, 1585, 1495, 1240, 740, and 685 cm^{-1}; nmr ($CDCl_3$) τ 2.50–3.00 (m), 3.50–3.94 (br d), 5.40 (quintet), 7.38–8.54 (m).

Anal. Calcd for $C_{11}H_{14}N_2S$: C, 64.04; H, 6.84; N, 13.58. Found: C, 64.80; H, 6.82; N, 13.65.

Allylcarbinyl Isothiocyanate (8).—The isothiocyanate was prepared by an adaption of the method of Jochims and Seeliger.[11] To a magnetically stirred solution of 10.30 g (0.05 mol) of *N*,*N*′-dicyclohexylcarbodiimide and 30 ml (38.0 g, 0.5 mol) of carbon disulfide in 100 ml of ether cooled at −20° was added dropwise 3.55 g (0.05 mol) of allylcarbinyl amine[10] in 5 ml of ether. The cooling bath was removed and the mixture was allowed to stir at room temperature for 47 hr. The precipitated thiourea was removed by filtration and triturated with ether. The combined ethereal solutions were vacuum evaporated to yield, after distillation, 4.35 g (77%) of **8**, bp 69.0–71.5° (16 mm) [lit.[10] bp 77.5° (28 mm)]. A portion of this material, further purified by preparative gc (6 ft × 0.5 in. LAC-728 column), had bp 67° (10 mm); ir (film) 2930, 2200, 2100, 1650, 1460, 1350, 995, and 925 cm^{-1}; nmr ($CDCl_3$) τ 3.76–4.48 (m), 4.58–5.00 (m), 6.41 (t), 7.53 (q).

Anal. Calcd for C_5H_7NS: C, 53.06; H, 6.23; N, 12.38. Found: C, 53.16; H, 6.30; N, 12.38.

1-Allylcarbinyl-3-phenylthiourea.—This derivative was prepared by treating 1.22 g (10.8 mmol) of **8** being stirred magnetically at room temperature with 1.0 g (10.8 mmol) of aniline. The mixture was allowed to stir overnight. The crude thiourea was crystallized from 50% ether–pentane, affording 1.98 g (89%). Three subsequent recrystallizations from 50% ether–pentane gave a sample of pure thiourea having mp 43.8–45.0°; ir (Nujol) 3300, 3175, 1320, 1300, 1240, 1200, 1100, 920, 840, and 780 cm^{-1}.

Cyclooctyl Isothiocyanate[25] (10).—To a magnetically stirred suspension of 20.8 g (0.1 mol) of dicyclohexylcarbodiimide and 100 ml of carbon disulfide in 100 ml of anhydrous ether being cooled in an ice–salt bath at −12°, was added dropwise a solution of 12.7 g (0.1 mol) of cyclooctyl amine in 50 ml of anhydrous ether. After all the amine had been added, the tempeature was allowed to rise slowly to room temperature and stirring was continued overnight. The resulting mixture was then combined with 10 g of Celite 545 filter aid and the precipitate was removed by filtration. The filter cake was washed three times with 100-ml portions of ether, and the filtrates were combined and concentrated. This afforded 17.3 g of a light orange liquid. The crude product was distilled at 83–85° (0.8 mm), yielding 16.0 g (94.7%) of a colorless liquid: mass spectrum (50 eV) *m/e* 169 (7.3), 111 (9.4), 69 (41), 55 (21), 44 (61), and 28 (100).

Product Studies.—Solutions 0.150 *M* in pure thiocyanate were prepared using acetonitrile, sulfolane, dimethylacetamide, or dimethylformamide. Aliquots (2 ml) were sealed in ampoules and heated at 130.0° (acetonitrile and sulfolane only), 140° (acetonitrile and sulfolane only), or 150.0° (all) for various times. The ampoules were quenched in ice water and opened, and the contents were poured into 25 ml of water. The resulting mixtures were extracted twice with 5 ml of pentane. The combined pentane extracts were washed with 10 ml of water, dried, and concentrated to yield residues which were anayzed by gc using the following columns and conditions: (A) column, 6 ft × 1/8 in. 30% PDEAS on Chromosorb W 60/80 mesh; temperature, 150°; carrier flow, 20 ml/min [R_t (min) **9**, 5.8; **8**, 6.3; **7**, 7.2; **6**, 8.1; **3**, 9.2; **5**, 9.9; **2**, 10.3; **1**, 14.1] and (B) column, 6 ft × 1/8 in. 20% LAC-278 on Chromosorb W 60/80 mesh; temperature, 110°; carrier flow, 60 ml/min [R_t (min) **8** and **7**, 3.4; **6**, 4.4; **3** and **2**, 5.6; **9**, 6.1; **1**, 8.6; **6**, 12.0].

Kinetic Procedure.—Solutions 0.150 *M* in pure **1**, **4**, or **5** were prepared in acetonitrile and sulfolane and treated as before. Reaction rates were obtained from plots of log [RSCN] *vs.* time by the method of least squares.

Catalyzed Isomerizations and Kinetics in Sulfolane.—Solutions 0.150 *M* in pure **1** were prepared using sulfolane which was either 0.01 or 0.10 *M* in potassium perchlorate or potassium thiocyanate. Aliquots (2 ml) were heated at 150.0° and treated as previously described.

Concentration Variation Studies.—Sulfolane solutions 0.015, 0.150, or 1.500 *M* in **1** were prepared. Aliquots (2 ml) were heated at 150° for 6 hr. The products were analyzed in the usual way.

Catalyzed Isomerizations and Kinetics in Benzene.—A 2% (w/v) solution of boron trifluoride ethereate in benzene was made 0.150 *M* in **1**. At intervals, 2-ml aliquots were withdrawn from the solution at reflux with a hypodermic syringe. The samples were washed with saturated sodium bicarbonate solution, dried, and concentrated to yield residues which were analyzed by gc.

Registry No.—**1**, 6129-85-7; **2**, 6068-88-8; **3**, 6068-89-9; **4**, 5263-57-0; **5**, 5263-56-9; **6**, 6068-90-2; **7**, 6068-91-3; **8**, 3386-97-8; **9**, 33522-03-1; **10**, 33522-04-2; 1-cyclopropylcarbinyl-3-phenylthiourea, 33522-05-3; 1-cyclobutyl-3-phenylthiourea, 33522-06-4; 1-allylcarbinyl-3-phenylthiourea, 33522-07-5.

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(25) O. Billeter, *Ber.*, **8**, 462 (1875).