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THE THERMAL ISOMERIZATION OF CYCLOPROPYLCARBINYL THIOCYANATE

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The isomerization of saturated alkyl thiocyanates has been a subject of rather infrequent investigation over the past century.[1] Recent studies of the benzhydryl system have provided information as to the course of isomerization of simple non-rearranging alkyl thiocyanates.[2] For a further exploration of thiocyanate isomerizations we have investigated the isomerization of cyclopropylcarbinyl* thiocyanate. We now wish to to report the preliminary results of this investigation. <u>This is the first observation of carbon skeleton rearrangements occurring concurrently with a thiocyanate-isothiocyanate</u> isomerization.

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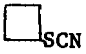
* This system was chosen because of the well documented[3] behavior of cyclopropylcarbinyl derivatives in reactions in which carbonium ions are generated.

Cyclopropylcarbinyl thiocyanate (I) was prepared from cyclopropylcarbinol via the p-toluenesulfonate ester (or chloride) followed by displacement by thiocyanate ion (95% yield). A completely homogeneous sample of I obtained by preparative g.c.) had b.p. 76.3-77.2° (14 mm), N_D^{25} 1.4937. Authentic samples of the isomeric cyclobutyl thiocyanate (II), N_D^{25} 1.4924*, and allylcarbinyl thiocyanate (III), b.p. 75.5-76.2° (18 mm), N_D^{25} 1.4845 were similarly prepared by displacement on the corresponding bromide (or p-toluenesulfonate) by thiocyanate ion. The isothiocyanates were obtained from the corresponding amines by their reaction with thiophosgene. Cyclopropylcarbinyl isothiocyanate (IV) had b.p. 78.0-79.0° (20 mm), N_D^{25} 1.5312, cyclobutyl isothiocyanate (V) had b.p. 77.4-78.5° (20 mm), N_D^{25} 1.5298, and allylcarbinyl isothiocyanate had b.p. 76.2-77.4° (21 mm), N_D^{25} 1.5177 (lit.[4] b.p. 77.5° (28 mm), N_D^{25} 1.5182). The structures of all compounds were supported by infrared and n.m.r. analysis.


I


II


III


IV


V


VI

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* Both cyclobutyl bromide and tosylate gave complex mixtures of isomers on attempted displacement by thiocyanate ion. Samples of pure II were therefore obtainable only in very low yields from preparative g.c.

Cyclopropylcarbinyl thiocyanate (I) was heated in a variety of solvents to determine the effects, if any, which these might have on the isomerization. The results of control experiments maintaining 0.15 M solution of I at 155° for 6 hours are shown in Table I.

TABLE I

Isomerization of Cyclopropylcarbinyl Thiocyanate
155°C, 6 hrs.

Solvent	% Isomerization
Benzene	0
Dioxane	<1
Nitrobenzene	5
Acetonitrile	15
Dimethylformamide	60
Sulfolane	68

The clearly enhanced reactivity in media of greater solvating power is in accord with the assumption that the isomerization proceeds via ions generated from the neutral thiocyanate molecule.*

The products of isomerization (determined by g.c.)** in acetonitrile are given in Table II.

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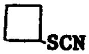
* It is conceivable that a cyclic concerted intramolecular isomerization could compete with ionic isomerization. Present results preclude the verification of the presence or absence of this process.

** The ratio of products was reproducible within the limits of experimental error. Overall material recovery was 95-99% on runs of 6 hrs. or less.

TABLE II

Isomerization Products of Cyclopropylcarbinyl Thiocyanate CH_3CN, 155°C

Product					
%	75	5	2	12	6

Attempts to isomerize thiocyanates II and III failed under conditions identical to those utilized for the isomerization of I. The product isothiocyanates IV, V, and VI, were likewise found to be stable under the reaction conditions. It is concluded that the observed isomerization products of I are the results of the primary dissociation process.

In an effort to verify the kinetic order of the isomerization, rate measurements were undertaken in dimethylformamide solution. Strict correspondence with first order kinetics was observed. The rate of isomerization at 154.7° ($2.55 \times 10^{-5} sec^{-1}$) is approximately one third of that reported for benzhydryl thiocyanate at 70° in the same solvent.[2c] The addition of potassium thiocyanate to the isomerizing mixture caused an acceleration of the rate similar to the "normal" salt effect reported for the isomerization of benzhydryl thiocyanates.[2d] Product ratios from isomerizations in dimethylformamide solution, 0.02 M to 0.2 M in potassium thiocyanate, were identical to those observed in the absence of the salt. Any appreciable contribution to the acceleration by bimolecular displacement of thiocyanate ion* was ruled out** in this manner.

Having established the isomerization of I as proceeding via a unimolecular process, the effects of added electrophiles were examined. The unique properties of this system seemed of value in developing a clearer explanation of the catalytic functions of these compounds. In experimental runs, 0.15 M solutions of I in 2% solutions of the catalyst in benzene were heated at reflux and the course of the isomerization followed by g.c. The results are given in Table III.

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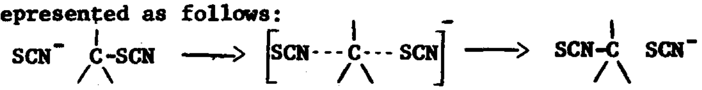
* Represented as follows:



$$SCN^- \ \overset{|}{\underset{/\ \backslash}{C}}\text{-}SCN \longrightarrow \left[SCN\cdots\overset{|}{\underset{/\ \backslash}{C}}\cdots SCN\right]^- \longrightarrow SCN\text{-}\overset{|}{\underset{/\ \backslash}{C}} \ \ SCN^-$$

(Recently reported studies utilizing benzyl thiocyanate and isotopically labelled thiocyanate ion have shown that displacement makes some contribution to isomerization in the benzyl system.)[2e]

** Bimolecular displacement should shift the product ratio in favor of IV.

TABLE III

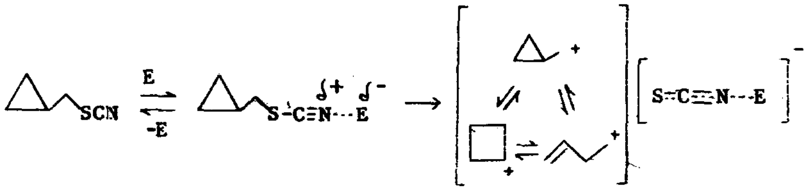
Products of the Isomerization of Cyclopropylcarbinyl Thiocyanate

Cat.	t 1/2	IV	V	VI	II	III
BF_3[a]	10 hrs.	8	6	1.5	57.5	27
$ZnCl_2$[a]	<1 hr.	8	8	1	52	31
-[b]	17 hrs.	75	5	2	12	6

[a] Benzene solvent at 80°

[b] CH_3CN solvent at 155°

The previously mentioned failure to obtain <u>any</u> isomerization of I, uncatalyzed in benzene at 155°C, is in marked contrast to these results. In addition, the large amount of II and III*, is drastically different from the predominant product, IV, obtained from the uncatalyzed reaction. The catalytic effect of the electrophile must be a result of its ability to coordinate with the nitrogen end of the thiocyanate group, thereby facilitating the dissociation of I. This is probably best represented as follows:



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* Control experiments showed that the rearranged thiocyanates II and III are inert under the conditions employed, as well as isothiocyanates IV, V, and VI.

The amount of thiocyanate products indicates that this coordination is of sufficient strength to provide for an extremely high degree of recombination involving the coordinated thiocyanate ion. All isothiocyanate products are likely derived from recombination involving "free" thiocyanate ion.

The rearrangements observed in the catalyzed and uncatalyzed isomerizations appear to be analogous to those observed in the carbonium ion reactions of cyclopropylcarbinyl halides, sulfonate esters, and amines.[3] Further investigation is directed toward understanding the behavior of the intermediate ionic species under various reaction conditions. The ultimate aim is to correlate these results with those already obtained for other thiocyanate and cyclopropylcarbinyl derivatives.

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