The Nature of the Carbonium Ion. IV. The σ-Route Norbornyl Cation from a Thiocyanate–Isothiocyanate Isomerization[1a]

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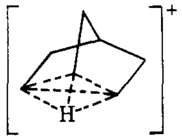
Abstract: *exo*-2-Norbornyl thiocyanate was isomerized to *exo*-2-norbornyl isothiocyanate in a variety of solvents. No *endo* products were detected. Isomerization of *exo*-2-norbornyl-2-*d* thiocyanate established that no 3,2- or 6,2(6,1)-hydride shifts occurred during the reaction. Similar observations of (−)-*exo*-2-norbornyl thiocyanate eliminated the possibility of a competing, concerted transformation. Rate measurements and catalytic effects of salts demonstrated the isomerization to be a first-order process and activation parameters were calculated. Experiments with ^{35}S-labeled thiocyanate ion provided evidence utilized in deducing the nature of the intermediates for isomerization.

Some of the most intricately examined rearrangements involving carbonium ions have been those of the 2-norbornyl cations generated from solvolytic and deamination reactions.[3] Interest has centered in large measure on the means by which various carbons of the bicyclo[2.2.1]heptyl skeleton are able, in effect, to change positions relative to the functional group during the reaction. Early explanations by Roberts, Lee, and Saunders[4] modified the original proposal by Winstein[5] that 1,2-carbon shifts were responsible for the totally racemic acetate obtained from optically active *exo*-2-norbornyl *p*-bromobenzenesulfonate upon acetolysis. Through isotopic tracer studies Roberts, *et al.*,[4] were able to demonstrate that 6,2- (and 6,1)-hydride shifts were also causes of the observed rearrangements. Accordingly, both the nortricyclonium ion[4] (**1**) and an interconverting set of bridged ions[5] (**2**) have been proposed as intermediates accommodating these observations.



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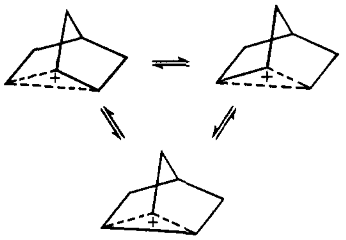

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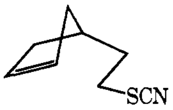
The situation becomes somewhat more complicated in less nucleophilic solvents where 3,2-hydride shifts also occur. First characterized[6] for a norbornyl cation in $SbF_5SO_2SO_2F_2$ and subsequently in formolysis of *exo*-2-norbornyl-2-*t* *p*-bromobenzenesulfonate,[7] these shifts were ultimately analyzed by the sophisticated tracer methods of Collins and Lietzke[8] who found them to be minor components of the overall rearrangement process. This essentially supported the results from nmr studies[6] indicating the rate of 3,2 shifts to be much slower than the rates of 6,2-hydride or 1,2-carbon shifts. As the latter two rates were still too rapid to be separable no conclusion was possible as to the existence of ions **1** or **2** in this weakly nucleophilic solvent.

Logically, a means of resolving this question seemed to be possible through a very rapid nucleophilic attack on the norbornyl cation. If the rates of hydride and carbon shifts could be at least partially exceeded by capture of a nucleophile, some indication of the relative rates might be gathered. Indication that this was at least possible for hydride shifts was to be seen in the results from solvolyses of *exo*-2-norbornyl-2-*d* *p*-trifluoromethylthiobenzoate by Smith and Petrovich.[9] This ester gave, presumably through internal return, *exo*-2-norbornyl *p*-trifluoromethylthiobenzoate in which the deuterium was equilibrated only between carbons 1 and 2. Evidence was therefore that a rapid reattack by the sulfur end of thiocarboxylate anion could completely preclude 6,2-hydride shifts but not 1,2-carbon shifts under proper conditions.

In the first paper of this series[10] we demonstrated that a thiocyanate ion generated by dissociation of 2-(Δ^3-cyclopentenyl)ethyl thiocyanate (**3**) could reattack the resultant π-route norbornyl cation (**4**) prior to complete electronic reorganization and lead to the isothiocyanate of retained structure, **5**. As this result was at odds with solvolysis results[11a] from the corresponding arylsul-



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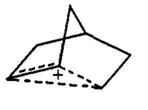

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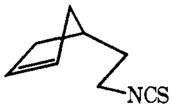

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[1] (a) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, P193; (b) to whom correspondence may be addressed at the Department of Chemistry, Brown University, Providence, R. I. 02912.

[2] National Institutes of Health Predoctoral Fellow, 1967–1970.

[3] For a comprehensive survey of the initial work in this area see: J. A. Berson in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 3.

[4] J. D. Roberts, C. C. Lee, and W. H. Saunders, *J. Amer. Chem. Soc.*, **76**, 4501 (1954); J. D. Roberts and C. C. Lee, *ibid.*, **53**, 5009 (1954).

[5] S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1147, 1154 (1952).

[6] M. Saunders, P. von R. Schleyer, and F. A. Olah, *ibid.*, **86**, 5680 (1964).

[7] C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 5355 (1966).

[8] C. J. Collins and M. H. Lietzke, *ibid.*, **89**, 6565 (1967).

[9] S. G. Smith and J. P. Petrovich, *J. Org. Chem.*, **30**, 2882 (1965).

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

[11] (a) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965), and references cited therein. (b) We are indebted to Professor Antonino Fava for supplying us with the unpublished results from solvolysis of 4,4′-dimethylbenzhydryl thiocyanate in 95% aqueous acetone at 25°. The rate of solvolysis under these conditions is nearly identical with the isomerization rate of this compound

Table I. Rates of Isomerization of **6** and **10**

Solvent	Temp, °C	Catalyst	**6** $k_t^{H\,a} \times 10^6$ sec^{-1}	**10** $k_t^{D\,a} \times 10^6$ sec^{-1}	$t_{1/2}$, hr
Diglyme	180.2		2.50 ± 0.30		77.0
	150.1		0.25 ± 0.08		760.0
Acetone			0.72 ± 0.20[b]		269.0
TMU[c]	150.4		1.15 ± 0.09		167.0
				1.20 ± 0.10	165.0
DMA[c]			2.53 ± 0.30[b]		76.2
DMF[c]			3.80 ± 0.20[b]		50.6
CH_3CN			4.25 ± 0.20[b]		45.2
Sulfolane	149.9		23.71 ± 0.08		8.1
	130.5		4.35 ± 0.04		44.2
				4.50 ± 0.40	41.0
		0.01 *M* KSCN	4.40 ± 0.04		44.8
		0.10 *M* KSCN	4.48 ± 0.08		44.8
		0.01 *M* $KClO_4$	4.98 ± 0.06		38.6
		ΔH^d = 29 kcal/mol	$\Delta S_{130.5}^d = -11$ eu		

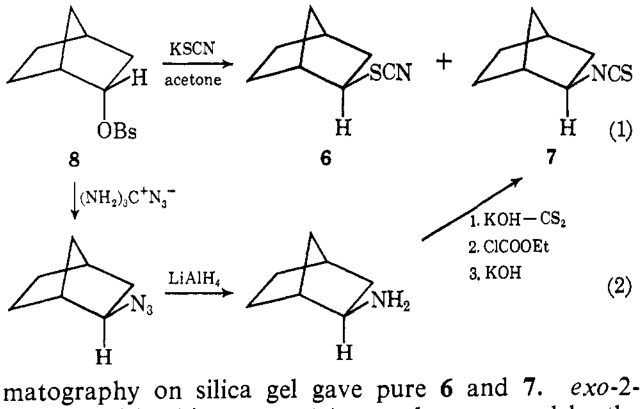
[a] k_t^H = rate of isomerization of **6**; k_t^D = rate of isomerization of **10**. [b] Calculated from two experimental determinations. [c] TMU = tetramethylurea; DMA = dimethylacetamide; DMF = dimethylformamide. [d] Sulfolane solution.

fonates, explanation could only be given involving extremely rapid collapse of the intermediate ion pairs.[10] Due however to the requirement that solvents for the isomerization be aprotic, we could not employ conditions identical with those of solvolysis. Nonetheless, the ionizing powers of acetonitrile, sulfolane, and dimethylformamide are at least comparable to those of the solvolytic aqueous acetone media;[11b] thus we felt that our inferences on ion pairs might not be totally restricted to our conditions. On this basis, an investigation of the thiocyanate-generated σ-route norbornyl cation appeared to offer the opportunity for a closer scrutiny of the rearrangement processes occurring after ionization of norbornyl derivatives.

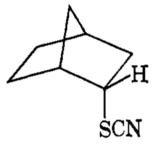
Results

exo-2-Norbornyl thiocyanate (**6**) was prepared by reaction of *endo*-2-norbornyl-*p*-bromobenzenesulfonate (**8**) with potassium thiocyanate in acetone. This procedure afforded a 3:1 ratio of **6** to isothiocyanate **7** (Scheme I, eq 1). Separation of this mixture by chromatography on silica gel gave pure **6** and **7**. *exo*-2-Norbornyl isothiocyanate (**7**) was also prepared by the reaction of carbon disulfide, ethyl chloroformate, and potassium hydroxide with the corresponding amine[10] (eq 2). The isothiocyanate **7** obtained in this manner was identical with the minor component of the potassium thiocyanate reaction with **8**.

Scheme I



Samples of *endo*-2-norbornyl thiocyanate (**9**) were synthesized by a method previously described.[10] For deuterium labeling studies, *exo*-2-norbornyl-2-*d* thiocyanate was prepared from *endo*-norbornyl-2-*d* *p*-bromobenzenesulfonate[9] by a reaction analogous to eq 1. Separation of the product mixture on silica gel gave



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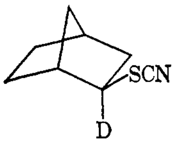

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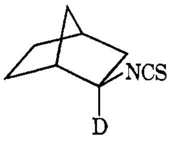

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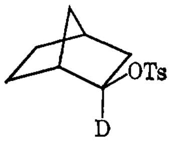

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thiocyanate **10** and isothiocyanate **11** which were shown by nmr analysis to contain, respectively, 0.84 and 0.85 atoms of deuterium in the *endo*-2 position. Since it was necessary for control experiments, *exo*-2-norbornyl-2-*d* *p*-toluenesulfonate (**12**) was prepared from its *endo* epimer[9] by acetate displacement, followed by lithium aluminum hydride reduction and treatment with *p*-toluenesulfonyl chloride. The ester **12** was shown by nmr to contain >0 96 atoms of deuterium in the *endo*-2 position.

Partially resolved **6** and **7** were obtained by thiocyanate ion displacement on (−)-**8** resolved by the method of Winstein.[5] This sequence afforded (−)-**6** calculated[12] to be 58.7 ± 6.0% optically pure and (+)-**7** calculated[12] to be 51.2 ± 6.0% optically pure.

Thiocyanate **6** isomerized at reasonable rates between 130 and 150° in most solvents. The only product detected was the isothiocyanate of retained structure, **7**, and this was completely stable to all reaction conditions studied. Table I summarizes the results from rate studies of the isomerizations of **6** and its deuterium labeled analog **10** in various aprotic solvents. The reactions were followed by glpc and by titration of standard *n*-butylamine which was consumed by the product iso-

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in acetonitrile at 25° as earlier reported by A. Iliceto, A. Fava, U. Mazzucato, and O. Rossetto, *J. Amer. Chem. Soc.*, **83**, 2729 (1961); (see also: A. Ceccon, A. Fava, and I. Papa, *Chim. Ind.* (Milan), **51**, 53 (1969)).

(12) Calculated on the basis of deuterium scrambling results from the previously mentioned preparation of 10 and 11.

Table II. Results of Deuterium Scrambling during Isomerizations of **10**

Solvent	Temp, °C	% rxn	R-SCN atoms C_2-*d*	R-NCS atoms C_2-*d*	$k_{ex}^{D\,a} \times 10^6$ sec^{-1}	$k_{ex}^{D\,a}/k_t^H$
Sulfolane	130.5	0	0.84		9.1 ± 2.0	2.10
		16	0.78	0.46		
		37	0.69	0.46		
		53	0.58	0.45		
		73	0.53	0.45		
TMU	150.7	0	0.84		3.5 ± 1.8	3.04
		10	0.79	0.47		
		24	0.68	0.48		
		45	0.53	0.50		
Diglyme	180.2	0	0.90		5.6 ± 1.8	2.24
		6	0.86	0.52		
		14	0.80	0.52		

[a] Rate of deuterium rearrangement from C_2 (to C_1).

Table III. Results from the Isomerization of (−)-**6** in Sulfolane at 130°

Time, hr	% reaction	(−)-R-SCN $[\alpha]^{25}$D (c = 10)[a]	(+)-R-NCS $[\alpha]^{25}$D (c = 10)[a]
0	0	−20.6 ± 0.3°	
8	11	−14.0 ± 0.4	0.1 ± 0.3
20	26	−10.1 ± 0.5	0.0 ± 0.5
35	45	−5.1 ± 0.3	−0.2 ± 0.4
57	60	−1.5 ± 0.4	0.0 ± 0.4
		$k_\alpha^b = 12.4 \pm 0.7 \times 10^{-6}$ sec^{-1}	$k_\alpha^b/k_t^H = 2.85$

[a] Measured in chloroform solution. [b] k_α = rate of loss of optical activity.

Table IV. Results of $^{35}SCN^-$ Competition Studies[a]

$t \times 10^3$, sec	2.64	7.50	12.06	19.08	30.30	45.90	66.42	159.5
% reaction	1.3	3.7	5.8	9.2	12.9	19.3	27.5	52.4
$A_{KSCN}{}^b$	997	992	986	978	955	931	931	910
$A_{RNCS}{}^b$	42.3	40.7	46.5	55.6	75.4	87.0	117	127
$A_{RSCN}{}^b$	1.0	2.5	5.5	8.9	13.9	24.0	34.3	110
$A_{mix}{}^{b,c}$	1.7	4.3	8.4	14.0	22.6	38.4	58.5	122
$F^d \times 10^2$	0.9	2.5	4.4	7.3	11.7	19.9	30.3	63.0

[a] Temperature, 130°; [RSCN] = 0.1 M; [KSCN] = 0.1 M. [b] Corrected for zero-time induced activity. [c] A_{mix} = activity of the recovered reaction mixture before separation. [d] F = fraction of exchange as calculated from the relationship A_{mix}/A_∞. A_∞ was estimated to be 193 by extrapolation of a plot of log A_{mix} *vs.* % reaction to 100% reaction.

thiocyanate after addition to the isomerized mixture.[13] The two analytical methods were mutually consistent and graphs (log [R-SCN] *vs.* t) of the data showed linear first-order behavior to a minimum of 60% reaction.

Table II summarizes the results found during isomerizations of **10**. Deuterium scrambling over the course of the reaction was followed by nmr and the results listed are averages of at least two trials. Within the limits of instrumental error we could find evidence for deuterium only at C_1 and C_2. The rates of rearrangement of deuterium (k_{ex}^D) refer then only to the equilibration of deuterium between these two positions on the norbornyl skeleton.

As control experiments *exo*-2-norbornyl *p*-toluenesulfonate and its deuterium labeled analog, **12**, were heated at 80 and 110° in the solvents considered with potassium thiocyanate. Under these nonisomerizing conditions, mixtures were isolated from sulfolane and diglyme which consistently contained 2:1 R-SCN:R-NCS, ratios, while TMU afforded a 1.5:1 ratio. The nmr analyses of deuterium labeled products recovered from sulfolane revealed 0.44 and 0.56 atoms of deuterium at C_2 in the thiocyanate and isothiocyanate, respectively.

The isomerizations of (−)-**6** were undertaken only in sulfolane since this solvent had been shown to give the cleanest results from the previous studies. Observations are tabulated in Table III. Each rotation shown is the average of twenty separate examinations of the chloroform solutions of product or reclaimed reactant.

In order to provide a more detailed view of the intermediates of isomerization, tracer studies were performed using ^{35}S-thiocyanate ion.[14] The intention was to establish a competition for the cation between the leaving group thiocyanate ion (organic thiocyanate) and labeled potassium thiocyanate (inorganic thiocyanate). In this fashion we hoped to obtain some measure of the degree of dissociation past the intimate pair stage.[15]

These experiments were performed by heating sulfolane solutions 0.1 M in potassium ^{35}S-thiocyanate and **6**. Table IV presents the specific activities of the inorganic thiocyanate (A_{KSCN}), organic thiocyanate (A_{RSCN}), and isothiocyanate (A_{RNCS}) recovered at various stages of the reaction. The specific activities are in arbitrary units with A_{KSCN} established as 1000 at zero time.

Since the limiting rate in the exchange process is the rate of formation of the intimate pair, k_i (see Discussion) the specific rate of exchange, k_{ex}, is dependent only on initial alkyl thiocyanate concentration. We therefore determined the gross rate of exchange[16] from a plot of ln (1 − F) *vs.* t and taking our initial [R-SCN] into account, $k_{ex} = 1.61 \times 10^{-6}$ sec^{-1}.

To determine the relative ratio between capture of the labeled thiocyanate ion S end and N end, the mixture was separated and the relative activities of the two components compared.[17] By this method k_S/k_N =

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(13) S. Siggia and J. G. Hanna, *Anal. Chem.*, 20, 1084 (1948).

(14) Prior to resorting to this method, studies were attempted utilizing azide, iodide, bromide, cyanide, and thiolacetate as competing nucleophiles for the exchange reaction. Iodide and azide ion could successfully compete with thiocyanate ion for the cation at high salt concentrations. However, separate experiments indicated *exo*-2-norbornylazide and iodide to be unstable to reaction conditions. Cyanide and bromide could never compete successfully with thiocyanate ion. Thiolacetate may have shown some ability to trap the cation, but underwent an exchange reaction with the organic thiocyanate in sulfolane even at nonisomerizing temperatures.

(15) A similar procedure has been applied to the benzhydryl system by A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Amer. Chem. Soc.*, 87, 1045 (1965).

(16) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1965, p 192.

(17) The comparison was accomplished utilizing the expression $k_S/k_N = A_{RSCN}(1 - \%\ \text{rxn})/A_{RNCS}(\%\ \text{rxn})$. Least-squares treatment of the first five points of k_S/k_N *vs.* t afforded a zero-time value of 2.0.

2.0, a close agreement with the results obtained from the previously described experiment utilizing **12** and thiocyanate ion in sulfolane at 80 and 110° (R-SCN/R-NCS = 2). It was therefore possible to calculate the limit of dissociation beyond the intimate pair stage. It follows from eq 3[15] that a maximum of 12% of the pairs go on to further separation.

$$k_{ex}k_N/k_t^H(k_S + k_N) = \text{fraction of dissociation ion pairs} \quad (3)$$

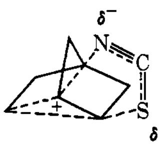
Discussion

There seems little doubt that this isomerization, like many of those previously investigated,[18] proceeds by way of unimolecular dissociation to a cation and thiocyanate ion. The resultant ions collapse regenerating the kinetically favored starting material or the thermodynamically preferred isothiocyanate. Certainly the acceleration of the reactions of **6** by polar solvents and dissolved salts indicates that this description of its isomerization is correct. We may concern ourselves therefore primarily with the behavior of the norbornyl cation with its ambident counterion.

The isolation of only one product, and the isothiocyanate of retained stereochemistry, **7**, eliminated all possibility that this cation possessed any features with regard to steric preference which were lacked by the solvolytic or deamination norbornyl intermediates. It had been previously shown[10] that the *endo*-2-norbornyl derivative, **9**, and its corresponding isothiocyanate were stable to the reaction conditions, thus we may assume that their absence is a reflection, not of competing isomerization processes, but of the commonly observed[3] partition of norbornyl ions. Establishing this feature left us free to examine the various rearrangements involved.

As evidenced from deuterium studies no 3,2-hydride shifts were detectable during the reaction. This is not surprising in that similar shifts are not observed even in acetolyses of the corresponding *p*-bromobenzenesulfonate.[5] More gratifying was the lack of evidence for 6,2- or 6,1-hydride shifts illustrating that the counterion was capable of reattack from the ion pair at a rate greater than that at which these shifts occur.[19a] This allowed us to separate out completely hydride shifts as contributors to any rearrangements observed. Because near perfect equilibration of deuterium between C_1 and C_2 occurred for all isothiocyanate products (and for thiocyanate recovered after two half-lives) there was proof that Wagner–Meerwein shift occurs at a rate well in excess of the rate of cation capture by thiocyanate ion. Fortunately the near equivalence of the rates of isomerization of C_2-deuterated thiocyanate **10** and undeuterated **6** eliminated the complication of a secondary α-deuterium isotope effect.[19b] The lack of any directing influence by deuterium on the cation was also established by the observation that **12** when treated with thiocyanate ion gives products with no hydride shifts but complete C_1–C_2 deuterium equilibration.

The competing possibility of a concerted transformation, such as is postulated in **13** could not be completely ruled out with deuterium labeling because of nmr error limits (4% by control experiments). This process should result in noticeable amounts of the inverted isothiocyanate product if it occurs at all. The detection only of completely racemic isothiocyanate in the more sensitive optical studies effectively eliminates **13** from consideration since only an unlikely equivalent but opposite process could lead to the total loss of optical activity observed.



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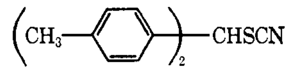

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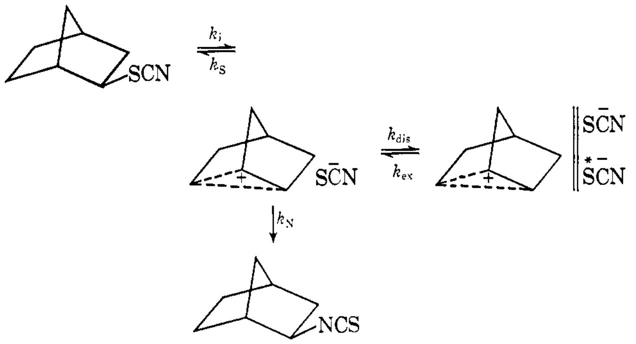
The ratios of deuterium equilibration and racemization rates to the isomerization rate in all solvents examined (see Tables II and III) were instructive in that they revealed even the sulfur end of the counterion to have no "memory" for the position from which it was expelled.[19b] The fact that the independently generated norbornyl cation (from **12**) gave a S end to N end preference ([R-SCN]/[R-NCS] = 1.5–2.0), which was always less than the values obtained for the above ratios, implied that even the initial ion pair possessed a cation symmetrical with respect to the anion. From logic, detection of an unsymmetrical cation by this means requires that the ratios k_α/k_t^H or k_{ex}^D/k_t^H be less than the S/N ratio.[19c] Considering the evidence accumulated, the norbornyl cation of isomerization seems most simply represented by the delocalized structures shown in Scheme II.

Scheme II



While the deuterium labeling and optical studies gave evidence that the isomerization must proceed through tightly bound ionic intermediates, the ^{35}S-tracer technique allowed a quantitative estimate of the extent of their separation. The ultimate results of these tracer experiments seem best accommodated by a pathway such as is shown in Scheme II. External radioactive thiocyanate ion can enter the norbornyl compounds

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[18] 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; (b) A. Fava in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Meyers, Ed., Pergamon Press, Oxford, England, 1966, p 73.

[19] (a) An estimate of 6×10^5 sec^{-1} to 6×10^6 sec^{-1} has been suggested for this rate in acetic acid; see E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 140. (b) The small inverse isotope effects revealed in Table I must be viewed with the experimental error taken into account. Certainly the magnitude of the k_t^H/k_t^D ratio is smaller than would be anticipated. We are, however, unable to distinguish between a temperature effect on this ratio and an indication of a high degree of intramolecular assistance to ionization (see C. C. Lee and E. W. C. Wong, *J. Amer. Chem. Soc.*, **86**, 2752 (1964)). (c) The failure to obtain equality between k_{ex}^D and k_α is the result of experimental error only. (d) This would indicate k_α and k_{ex}^D to be less than the rate of ionization, thereby showing a preference for C_2 by sulfur end in its return to the cation.

only from some stage of dissociation past the intimate ion pair. The lack of complete equilibration of radioactivity between ionic and covalent thiocyanates (see Table IV) is, however, a first indication that the major portion of the reaction does not proceed to this exchanging stage. It was possible nevertheless to estimate the degree of dissociation from the amount of ^{35}S-incorporation which did take place. The calculated value of 12% for dissociation of intimate pairs is interesting when compared with the behavior of pairs from 4,4′-dimethylbenzhydryl thiocyanate (**14**).[15] We were able to estimate 19% as a likely limit for their dissociation from the data of Fava and Iliceto[15] at 0° in acetonitrile (after extrapolation to 0.1 M salt concentration). Observation that the degree of separation is less for the norbornyl system is reasonable in light of the greater stability of the 4,4′-dimethylbenzhydryl cation which should permit higher fractions of dissociation. The surprisingly small difference between these values is tempered, however, when one considers the 130° temperature spread between the two conditions employed. Further, the results from **14** were obtained in the less polar acetonitrile while the norbornyl isomerizations were examined in sulfolane. In light of the known[15] sensitivity of the rate of exchange, k_{ex}, to solvent ionizing power and temperature, it seems likely that under identical conditions, the difference in degree of dissociation would be even more pronounced. The close relationship between carbonium ion stability and ionic separation should thereby be revealed.

Knowledge of the k_S/k_N ratio[20] allowed estimation of the rate of ionization, k_i. The relationship[15] $k_i = (k_S + k_N/k_N)k_t^H$ afforded a value of 13.0×10^{-6} sec^{-1}. Since, within error, $k_i = k_\alpha = k_{ex}^D$ (in sulfolane), it is suggested that the processes giving rise to racemization and deuterium scrambling are limited only by the rate of ion pair formation. This is in excellent agreement with the previous results showing a failure of sulfur end "memory" due to the immediate acquisition of symmetry by the cationic portion of the ion pair.

In order to examine the norbornyl cation further by trapping techniques a reaction is required which must involve a greater degree of intimacy of the ion pairs than the 88% observed here, as well as a nucleophile of greater strength than the sulfur end of thiocyanate. We look forward to future studies in this area.

Experimental Section[21]

exo-**2-Norbornyl Thiocyanate (6).** Synthesis of **6** was accomplished by the procedure of Spurlock and Cox[10] in 35–45% yield, bp 79–82° (1.35 mm) [lit.[10] bp 81–84° (1.9 mm)]. Infrared and nmr spectra were identical with those reported.

exo-**2-Norbornyl Isothiocyanate (7).** The previously described procedure[10] afforded **7** in 70% yield, bp 80–82° (1.8 mm) [lit.[10] bp 81–83° (2 mm)]. Infrared and nmr spectra corresponded to those reported.

1,3-(1-Adamantyl-*exo*-2-Norbornyl)thiourea. To a solution of 1.07 g (7 mmol) of a mixture of *exo*-2-norbornyl thiocyanate and isothiocyanate in 20 ml of anhydrous dioxane was added 1.41 g (9.4 mmol) of 1-adamantyl amine freshly prepared from its hydrochloride. The reaction mixture was stirred overnight, added to 50 ml of water and extracted with three 15-ml portions of pentane. The pentane extracts were combined, washed successively with 10% hydrochloric acid and saturated sodium bicarbonate solution, and dried. Evaporation of the solvent afforded 0.820 g (5.4 mmol) of thiocyanate, **6**. The aqueous layer after pentane extraction contained a white solid suspension and so was acidified with hydrochloric acid and extracted with three 40-ml portions of ether. The ether extracts were combined and washed successively with water, 10% sodium hydroxide, and water. Drying, followed by concentration of the solution to 10% of its original volume and addition of pentane precipitated the thiourea. Three recrystallizations from ether–pentane afforded 0.362 g (1.2 mmol) of 1-(1-adamantyl)-3-(*exo*-2-norbornyl)thiourea (mp 163.5–164°); infrared spectrum ($CHCl_3$) 3400, 1725, 1525, and 1090 cm^{-1}.

Anal. Calcd for $C_{18}H_{28}N_2S$: C, 71.00; H, 9.27; N, 9.20; S, 10.53. Found: C, 71.15; H, 9.13; N, 9.29; S, 10.43.

exo-**Norbornyl-2-*d* Thiocyanate (10) and *exo*-Norbornyl-2-*d* Isothiocyanate (11).** *endo*-Norbornyl-2-*d* *p*-bromobenzenesulfonate prepared by the method of Smith and Petrovich[9] was shown by nmr to have <0.02 atom of hydrogen at C_2. Reaction of 42.8 g (0.12 mol) of this ester with 40.5 g (0.24 mol) of tetraethylammonium thiocyanate[22] in a procedure analogous to that used for the synthesis of the undeuterated material afforded 9.73 g (0.06 mol) of a mixture of the thiocyanate **10** and isothiocyanate **11**. The mixture was chromatographed on a 250-g silica gel column, and elution with pentane afforded 3.84 g (39%) of pure **11**, shown by nmr to contain 0.84 atom of deuterium at the 2-*endo* position. Further elution with ether gave 6.00 g (60%) of pure **10** shown by nmr to have 0.85 atom of deuterium at the 2-*endo* position.

Anal. (**10**) Calcd for $C_8H_{10}DNS$: C, 62.31; H, D, 7.83; N, 9.09. Found: C, 62.31; H, D, 7.66; N, 9.28.

Anal. (**11**) Calcd for $C_8H_{10}DNS$: C, 62.31; H, D, 7.83; N, 9.09. Found: C, 62.05; H, D, 7.72; N, 9.18.

Reaction of Thiocyanate Ion with *exo*-Norbornyl-2-*d* *p*-Toluenesulfonate (12).[24] To a solution of 0.52 g (1.95 mmol) of **12** in 13 ml of sulfolane was added 0.73 g (3.9 mmol) of tetraethylammonium thiocyanate. This solution was sealed in a tube and heated at 80° for 24 hr. Work-up of the reaction mixture as described above followed by glpc analysis showed it to contain 33% isothiocyanate and 67% thiocyanate. Separation of these components on a 25-g silica gel column afforded 0.04 g of the former and 0.05 g of the latter. Nmr analysis of the thiocyanate indicated it to have 0.46 atom of deuterium at C_1 and 0.54 atom of deuterium at C_2. Similar examination of the isothiocyanate showed it to contain 0.49 atom of deuterium at C_1 and 0.51 atom of deuterium at C_2.

(−)-*exo*-2-Norbornyl Thiocyanate ((−)-6) and (+)-*exo*-2-Norbornyl Isothiocyanate. ((+)-7). Partially resolved *endo*-2-norbornyl *p*-bromobenzenesulfonate $[\alpha]^{25}D$ 8.87 ± 0.24° (c = 10; 75.3% optical purity) was prepared by the method of Winstein and Trifan.[5] Reaction of this material with 6.66 g (0.04 mmol) of tetraethylammonium thiocyanate in 30 ml of anhydrous acetone afforded 2.40 g (89.1%) of a mixture of **6** and **7**. Separation of the mixture, accomplished by chromatography on 36 g of silica gel, gave 1.104 g (7.2 mmol; 48%) of **6**, $[\alpha]^{25}D$ −20.6 ± 0.3° (c 10.3; 58.7 ± 6.0% optical purity[12]), and 0.667 g (4.35 mmol; 24.6%) of **7**, $[\alpha]^{25}D$ 3.7 ± 0.2 (c 11.95; 51.2 ± 6.0% optical purity[12]).

Kinetic Procedures. Five-milliliter aliquots of sulfolane, diglyme, or tetramethylurea solutions, 0.04 M in isomerized material were analyzed by the previously reported titration procedures.[10] Comparable results were obtained by the following alternate method of analysis. Solutions 0.15 M in thiocyanate were

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(20) Unfortunately we have insufficient data to easily compute absolute values for k_S and k_N. These would clearly be desirable since they provide limits for the rates of 6,2- (6,1)-hydride shifts in this medium and 1,2-carbon shifts (if indeed they do occur).

(21) 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. Optical rotation measurements were accomplished with a Kern Full-Circle polarimeter using a 1-dm tube. The tracer activities were measured using a Beckman CPM-100 liquid scintillation system. The scintillation fluid consisted of a solution of 4.0 g of 2,5-bis[2-(5-*t*-butylbenzoxazolyl)]thiophene (BBOT) and 60 g of naphthalene dissolved in 288 ml of xylene, 288 ml of dioxane, and 174 ml of absolute ethanol.

(22) Tetraethylammonium salts were used since it was determined that there was less deuterium scrambling with these reagents than with the corresponding potassium salts. These quaternary ammonium salts were prepared by the method of Longo.[23]

(23) F. R. Longo, J. D. Kerstetter, T. F. Kumosinski, and E. C. Evans, *J. Phys. Chem.*, 70, 431 (1966).

(24) Compound **12** was prepared by treatment of its *endo* epimer[9] with tetraethylammonium acetate followed by lithium aluminum hydride reduction of the resultant acetate and reaction of the *exo*-norbornanol-2-*d* product with *p*-toluenesulfonyl chloride. Nmr of **12** showed it to contain >0.96 atom of deuterium at C_2.

prepared in the appropriate solvent. One milliliter aliquots were sealed in tubes and heated at 130 or 150°. Tubes were quenched in ice water at various intervals, their contents poured into 20 ml of water, the products extracted with three 4-ml portions of pentane, and the combined extracts dried and concentrated. The residues were analyzed by glpc using a 2-ft 15% diethylene glycol succinate on Chromosorb W column. At 120° and a helium carrier flow of 50 ml/min, **6** and **7** showed retention times of 14.0 and 8.2 min, respectively. The analogous deuterated compounds **10** and **11** gave similar results on this column. Isomerizations in the presence of potassium thiocyanate or potassium perchlorate were analyzed by the same procedure.

Deuterium Labeling Experiments. Solutions of **10** were made up in sulfolane, TMU, or diglyme using quantities such that at least 0.08 g of isothiocyanate would be produced after the isomerization interval. The appropriate solutions were sealed in glass tubes and heated at 150 ± 0.1°. Tubes were removed at various time intervals and worked up in the previously described manner. Separation of the crude isomerization mixture and analyses of the components were carried out as described before.

Isomerization of (−)-*exo*-2-Norbornyl Thiocyanate ((−)-6). A 1.029 g (6.73 mmol) sample of (−)-**6** was dissolved in 45 ml of sulfolane, sealed in a tube, and heated at 130 ± 0.1° for 8 hr (10.9% isomerization). The tube was quenched in ice water and worked up in the usual manner. Separation of the crude mixture on silica gel followed by distillation afforded pure thiocyanate and isothiocyanate, whose respective optical rotations were measured. This procedure was repeated with samples heated for 20.0, 35.0, and 57.0 hr (26%, 45%, and 77% reaction, respectively; see Table III).

Tracer Studies. A solution 0.1 *M* in potassium thiocyanate-^{35}S and in **6** was prepared by dissolving 3.81 mg of potassium thiocyanate-^{35}S (specific activity = 27.3 mCi/mmol), 96.09 mg of potassium thiocyanate, and 153 mg of **6** in 10 ml of sulfolane. One milliliter aliquots of the resultant solution were sealed under nitrogen in ten tubes and heated at 130.1°. The tubes were quenched at regular intervals (see Table IV). Extent of isomerization was measured by analysis of control tubes containing 0.1 *M* solutions of nonradioactive thiocyanate ion and **6**.

To each tube containing-^{35}S thiocyanate were added known amounts of unlabeled **6** and **7** as carriers. The resultant mixture was then poured into exactly 25.0 ml of water and extracted three times with 5-ml aliquots of pentane. The water solution was saved for analysis to determine the amount of remaining ionic ^{35}S thiocyanate.

The combined pentane extracts were washed two times with 5 ml of water, dried, and the solvent evaporated. The mixture activities reported in Table IV were determined from accurately weighed amounts of this purified product. To effect separation of thiocyanate and isothiocyanate, each mixture was then treated with aniline in a procedure analogous to that reported for preparing the 1-adamantylthiourea derivative of 7. Work-up afforded **6** and 1-phenyl-3-*exo*-2-norbornylthiourea. The R-SCN activities reported were found by analyzing known weights of **6** recovered for the above reaction. Isothiocyanate activities were acquired from analyses of the aniline thiourea derivatives after their recrystallization from ether–pentane.

Activity of ionic thiocyanate was measured utilizing a 5 μl aliquot of each water sample. The remaining water solution was then extracted twice with ether, its volume measured, and another 5-μl sample analyzed. This procedure was repeated to constant activity.

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Preparation and Characterization of Tyrosine and Lysine Metal Chelate Polyesters and Polyamides[1]

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Abstract: Polyesters and polyamides of bis(tyrosinato)metal(II) (M = Cu, Ni) and bis(lysine)metal(II) dichloride (M = Cu, Zn) complexes have been synthesized by interfacial polycondensation with aryl diacid chlorides. The presence of unhydrolyzed acid chloride end groups in the products indicates that the degree of polymerization is governed by the insolubility of the products in both phases. Using a semiquantitative determination of the organic compounds obtained upon removal of the metal ion, the degree of polymerization is estimated to be four to five. This removal has led to the characterization of the following new organic compounds: O,O′-2,5-dichloroterephthaloyldityrosine, O,O′-terephthaloyldityrosine, O,O′-isophthaloyldityrosine, ε-N,ε-N′-2,5-dichloroterephthaloyldilysine, ε-N,ε-N′-terephthaloyldilysine, and ε-N,ε-N′-isophthaloyldilysine.

There are three fundamentally different synthetic approaches which lead to chelate polymers: (1) the reaction of metal ions with bischelate ligands, (2) the chelation of metal ions by an existing polymer,[2-5] and (3) the polymerization of metal chelates containing free functional groups.[6,7]

We have used the third approach and the interfacial polymerization technique to prepare polyamides and polyesters of the general types I–IX. We have also determined the degree of polymerization by semiquantitative determination of the organic compounds obtained when the metal ion is removed.

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