The Nature of the Carbonium Ion. VII. The Dehydronorbornyl Cations from Thiocyanate Isomerizations

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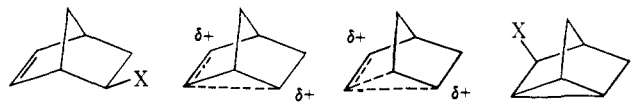
Abstract: The thiocyanate isomerization technique for trapping carbonium ions was applied to the intermediates from the 5-norbornenyl–nortricyclyl series. *exo*-5-Norbornenyl (**6**) and nortricyclyl (**8**) thiocyanates were studied during thermal isomerizations in several aprotic solvents. Unlike the solvolytic reactions of analogous halides or arylsulfonate esters, relative proportions of products from **6** and **8** were quite different in almost all cases. The norbornenyl derived product mixtures tended to contain substantially greater amounts of the unrearranged *exo*-5-norbornenyl isothiocyanate **7** than was ever detected from the nortricyclyl starting material. The reverse was true for **8** where nortricyclyl isothiocyanate **9** was produced in larger quantities than from **6**. Interconversions of the thiocyanates **6** and **8** provided a third component of product mixtures, but in no instances were the *endo*-5-norbornenyl isomers **10** and **11** isolated. Solvent and catalyst studies indicated the isomerization rates to be solvent dependent, and the product ratios to be only slightly affected by changes in solvent polarity or additions of ionic salts. Reaction rates and activation parameters were consistent with the notion that the first formed intermediates are ion pairs in which the cation resembles the solvolysis cation. An overall interpretation of the results is proposed involving ion pair intermediates in which special attention is given to the position of the anion relative to the faces of the cation.

In previous papers of this series[3] we have demonstrated the utility of the thiocyanate isomerization technique for examination of ion pairs[4] in the study of easily rearranged cationic intermediates. The main restriction of this technique—that the alkyl thiocyanate receives intramolecular assistance to ionization if the substituent is primary or secondary—has strongly dictated our choices of alkyl systems to investigate. In particular we have devoted ourselves to studies of those bridged bicyclic derivatives whose analogous arylsulfonate esters are reported to solvolyze with internal assistance by a π[3a,c,d] or σ bond.[3b,c] Finding that there are indeed parallels between the behaviors of the cationic portions of the thiocyanate-generated ion pairs and the cations of solvolyses, we have been drawn toward investigations of cations which we suspect will be more advantageously studied by restricting their lifetimes through the rapid collapse of ion pairs. A natural consequence of this direction was arrived at with the C_7-substituted norbornenyl and thiocyanates which were subjected to study in order to ascertain more about the relationship of skeletal stability to the migratory aptitude of the counterion in the ion pair.[3d] It was apparent from this work that the skeletal partition of the cation is in some measure governed by the continuing proximity of the thiocyanate ion to the site from which it was generated. Accurate estimates of this effect were unfortunately negated by the extreme instability of the rearranged tricyclic skeleta relative to the original bicyclic ones. Only broad limits were in fact discernible.

To overcome the disadvantage of skeletal relationship we have continued our evolution of structural effect studies with the norbornenyl cations from *exo*-5-norbornenyl **1** and nortricyclyl **4** derivatives. In this case, because of the greater stability of the tricyclic skeleton, it appeared that we might be rewarded



1 2 3 4

with a clear answer to the question raised by the 7-norbornenyl results. Perhaps most intriguing was the distinct possibility of reversing the normal partition of ions related to **2** and **3**. These ions, proposed[5] as intermediates for the solvolyses of **1** and **4** (X = arylsulfonate, halide), have demonstrated a marked favoring of the tricyclic skeleton upon nucleophilic attack during solvolyses. Actually, they lead in almost every instance to a great predominance (>88%) of nortricyclyl **4** product. For the ions of isomerization, it is obvious that this need not be the case since the anticipated minimal cation–anion separation should give a greater tendency for collapse at the original site of attachment. Any reluctance to migrate by the thiocyanate portion of the ion pair generated from the 5-norbornenyl derivative **1** should thus be visible in a lessening of the nortricyclyl:norbornenyl product ratio.

For this reason, we synthesized the four isomeric bicyclo[2.2.1]hept-2-en-5-yl (5-norbornenyl) derivatives

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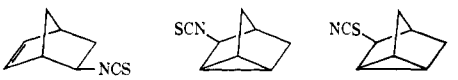
(2) From the thesis submitted by W. G. Cox in fulfillment of the requirements for the M.S. degree, Temple University, 1969.

(3) (a) L. A. Spurlock and W. G. Cox, *J. Amer. Chem. Soc.*, **91**, 2961 (1969); (b) L. A. Spurlock and T. E. Parks, *ibid.*, **92**, 1279 (1970); (c) L. A. Spurlock and R. J. Schultz, *ibid.*, **92**, 6302 (1970); (d) L. A. Spurlock and Y. Mikuriya, *J. Org. Chem.*, in press.

(4) For recent reviews see: 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., p 161; A. Fava in "Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. T. Meyers, Ed., Pergamon Press, Oxford, p 73.

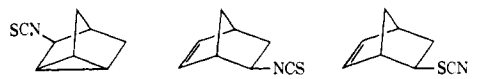
(5) (a) S. Winstein and E. Kosower, *J. Amer. Chem. Soc.*, **81**, 4399 (1959); (b) S. Winstein, *Experientia, Suppl. II*, 137 (1955); (c) J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, 77, 3034 (1955); (d) S. Winstein, *Bull. Soc. Chim. Fr.*, **18**, 55 (1951); (e) S. Winstein, H. M. Walborsky, and K. C. Schreiber, *J. Amer. Chem. Soc.*, **72**, 5795 (1950); (f) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

Table I. Isomerizations of 0.17 *M* Solutions of *exo*-Bicyclo[2.2.1]hept-2-en-5-yl Thiocyanate (**6**) at 150°

Solvent	Catalyst (*M*)	Time, hr	Relative product ratio 	% isomerization
Sulfolane		12	49 26 25	49
		0.9	41 20 39	6
	KSCN			
	(0.1)	20	41 25 34	74
		12	39 21 39	53
		8	40 22 38	44
	(0.01)	12	48 22 30	48
	$KClO_4$			
	(0.1)	12	19 39 42	76
	(0.01)	12	42 28 30	49
CH_3CN		12	38 18 44	11
		5	38 17 45	6
DMF[a]		12	43 14 42	9
		7	7 Trace 93	3
MEK[a]		12	23 77	1
		39	53 12 36	3
Diglyme		12	20 80	1
		104	50 16 34	3
Benzene[b]	BF_3			
	(0.3)	12	13 84 3	99

[a] DMF = dimethylformamide; MEK = methyl ethyl ketone. [b] Temperature = 80°.

Table II. Isomerizations of 0.17 *M* Solutions of Tricyclo[2.2.1.$0^{2,6}$]heptan-2-yl Thiocyanate (**8**) at 150°

Solvent	Catalyst (*M*)	Time, hr	Relative product ratio 	% isomerization
Sulfolane		72	91 7 2	43
		46	88 8 4	33
		22	88 8 4	23
		6	82 9 9	9
	KSCN			
	(0.1)	70	87 11 2	59
		46	85 10 5	41
		22	82 12 6	28
	$KClO_4$			
	(0.1)	46	93 5 2	59
	(0.01)	46	90 7 3	39
CH_3CN		46	85 6 9	9
		22	83 7 11	6
Benzene	BF_3			
	(0.3)	24	89 11	96

and the two tricyclo[2.2.1.$0^{2,6}$]hept-3-yl (nortricyclyl) derivatives with S-bound (thiocyanate) and N-bound (isothiocyanate) thiocyanate functionality, and subjected them to thermal studies.

Results

exo-Bicyclo[2.2.1]hept-2-en-5-yl thiocyanate (**6**) was prepared by tetraethylammonium thiocyanate displacement on *endo*-bicyclo[2.2.1]hept-2-en-5-yl *p*-bromobenzenesulfonate[5e] in acetone. This reaction actually produced a mixture consisting of thiocyanate **8** and isothiocyanates **7** and **9**, along with the predominant amount of the desired **6**. The thiocyanates were separated from the isothiocyanates by chromatography on silica gel and pure **6** was obtained by preparative gc. Authentic samples of *exo*- and *endo*-bicyclo[2.2.1]hept-2-en-5-yl isothiocyanates (**7** and **11**, respectively) were synthesized simultaneously from a 40:60 mixture of the corresponding amines[6] *via* the conventional[3a] carbon disulfide–*N*,*N*′-dicyclohexylcarbodiimide method. The pure isothiocyanates were obtained through gc separation. *endo*-Bicyclo[2.2.1]hept-2-en-5-yl thiocyanate (**10**) was afforded by treatment of a mixture of the *exo*- and *endo*-thiols[3a] with cyanogen chloride. As before the mixture of thiocyanates was separated by gc and the minor component in this case confirmed as identical with the previously prepared *exo*-thiocyanate **6**. Tricyclo[2.2.1.$0^{2,6}$]hept-3-yl thiocyanate (**8**) was obtained from 3-nortricyclyl *p*-bromobenzenesulfonate,[5e] and tricyclo[2.2.1.$0^{2,6}$]hept-3-yl isothiocyanate (**9**) was obtained from 3-nortricyclylamine[7] in procedures analogous to those used for **6** and **7**, respectively. Isomer homogeniety in excess of 98.5% was obtained in every case and all structures were confirmed by infrared, nmr, and elemental analyses.

Tables I and II summarize the influences of solvents and catalysts on product distributions and isomerization rates of **6** and **8**. These results were verified by com-

(6) W. E. Parham, W. T. Hunter, and R. Hanson, *J. Amer. Chem. Soc.*, 73, 5068 (1951).

(7) See Experimental Section.

parisons of the gas chromatographic retention times displayed by the components of the mixtures with those of independently prepared authentic samples on two columns of different liquid phase. Values listed are the averages of at least three runs with overall material recoveries of 96–99%. Stabilities of the products, and the undetected endo isomers **10** and **11**, to the reaction conditions were checked in control experiments employing the individual components. Other than the two thiocyanates **6** and **8** (whose dual isomerizations have obvious influences on product distribution) only the *exo*-norbornenyl isothiocyanate **7** showed any tendency to isomerize. Quite unusually, this compound converted very slowly to nortricyclyl isothiocyanate **9** in sulfolane solution. As the transformation was only to the approximate extent of 5% after 24 hr at 150°, its influence on the product distributions from the much more rapidly isomerizing **6** is probably negligible. In the case of **8**, which isomerizes more slowly, the small decrease in the **7**:**9** ratio discernible with extended time (Table II) may be due to this secondary skeletal rearrangement.

Concentration effects were examined by analyzing isomerization mixtures from 1.7 and 0.017 *M* solutions of **6** in sulfolane, acetonitrile, and dimethylformamide. The very concentrated solutions showed some rate retardation and changes in product distribution attributable to the effects of weakened ionizing power of the solvent. By contrast, the most dilute solutions gave no appreciable differences in rates or product distributions from those shown by the usually employed 0.17 *M* solutions; thus we felt justified in the standard utilization of this concentration.

The effects of ionic salts on the isomerizations of **6** and **8** were studied by addition of appropriate amounts of these materials to solutions otherwise identical with the usual isomerization media. The results of the studies also appear in Tables I and II along with those from the treatment of **6** and **8** with boron trifluoride in benzene solution. The latter results are striking in that these thiocyanates, like most of those previously investigated,[3,4] undergo no detectable isomerization in benzene, even at 150°, in the absence of catalysts. The isothiocyanates **7** and **9** were unchanged by the Lewis acid through the time of examining the isomerization, and in fact through an additional 72 hr of control, thereby confirming their ratio as the result of a primary process.

Listed in Table III are the results from rate studies of

Table III. Rate Studies of the Isomerizations of **6** and **8** in Sulfolane

RSCN	Temp, °C	$k \times 10^6$, sec^{-1}	$t_{1/2}$, hr	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
6	150.0	10.9 ± 0.5	16		
	130.0	1.8 ± 0.2	110	31	−8
8	150.0	2.5 ± 0.1	77		
	130.0	0.43 ± 0.1	443	30	−15

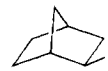
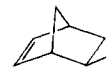
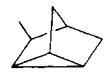
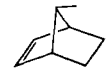
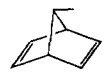
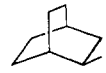
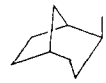
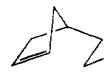
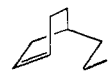
6 and **8**. Runs in solvents other than sulfolane were not consistent, and are not reported.[8] The isomerizations were followed by gc, and the rates obtained from plots of log [relative mole fraction RSCN] *vs.* time. These plots were linear to a minimum of 43% reaction for **6** and 38% reaction for **8**. The values shown, which are the averages of at least three runs, are therefore obtained from these phases of the reactions

(8) As this irreproducibility is common for slow isomerizations at 150° we attribute it as before to decomposition effects.

Discussion

The kinetic order and relative rates of isomerization of both thiocyanates lend further support to a simple ionization as the initial step of isomerization. Amplifying this observation, in Table IV the relative rates of

Table IV. Comparison of Relative Thiocyanate Isomerization Rates in Sulfolane with *p*-Toluenesulfonate Acetolysis Rate

Alkyl group	RSCN rel rate, 150°	ROTs rel rate, 25°
	1	1[b]
	0.46	0.51[b]
	0.11	0.17[b]
	100[a]	8×10^4
	1×10^4[a]	8×10^6[c]
	0.19	0.83
	0.11	0.48
	0.21	0.04
	0.02	3×10^{-3}[b]

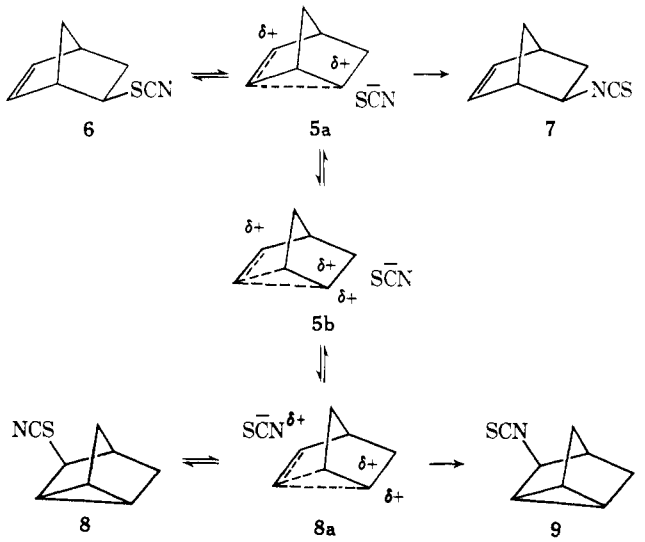
[a] Extrapolated from data at other temperatures. [b] Extrapolated from data of ROBs. [c] Estimated from values listed for RCl.

several previously examined thiocyanates and the present ones are compared with the relative rates of acetolysis for the *p*-toluenesulfonates of the same structure. The identical relative orders, despite the greatly divergent conditions of isomerizations and solvolyses, allow further belief that deductions drawn concerning the ionic intermediates of one reaction will be, in the main, applicable to the other.[9] We have therefore continued our practice of assuming that the accepted cations of solvolyses are structurally analogous to those of isomerizations. The differences in behavior between these ions of different source must be primarily due to the strong influence of thiocyanate ion in the ion pairs of isomerization. With emphasis therefore on the relative positions of the cation and anion, we propose in Scheme

(9) The apparent compression of the thiocyanate rates is most easily explained through the assumption of a transition state for isomerization in which the alkyl and thiocyanate groups are more closely associated than are the alkyl cation and arylsulfonate anion in the acetolysis transition state.

I an overall reaction pathway for thiocyanates **6** and **8**

Scheme I

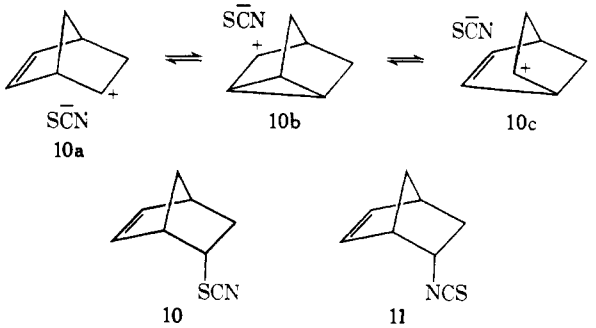


which can account for the observed product distributions and catalytic effects.

To maintain consistency with the acetolyses of isotopically labeled **1**-OBs,[5c] it must be assumed that the initially obtained intermediate from the *exo*-norbornenyl thiocyanate **6** contains the unsymmetrical dehydronorbornyl cation **5a**. The anion necessarily resides close to the site of detachment in this early phase of ionization. Formation of large quantities of unrearranged isothiocyanate **7** is thus not surprising since it is likely that collapse of **5a** would be quite rapid. The actual product distributions from **6** give some indication of the rates of cation–anion migration relative to those of collapse to unrearranged structure (see Table I). Apparently migration is somewhat faster in sulfolane but shifts toward equality with the collapse rate in solvents of lower polarity. This is most easily explained as a solvation phenomenon. Other experiments indicate that the dehydronorbornyl cation, in absence of large counterion effects, to favor the nortricyclyl over the norbornenyl skeleton by an approximate 88:12 ratio.[10] From this it can be calculated that in sulfolane to 6% isomerization, a *minimum* of 33% of the non-self-regenerating[11] ion pairs obtained from **6** do not undergo appreciable cation–anion migration prior to collapse to products. In order to explain the additional formation of nortricyclyl products it is necessary to invoke at least one more ion pair. The choice of the symmetrical cation in **8a** is again by analogy to the results from labeling studies of acetolysis,[5c] where the unsymmetrical ion **2** was demonstrated to rapidly convert to the symmetrical ion **3** (or its equivalent). It therefore seems logical that from **5a**, migration of thiocyanate ion to the opposite face of the cation might also be accompanied by this stabilizing electronic reorganization of the positive species. Since **8a** may also serve as the initially derived intermediate from **8**, its use as a product-forming intermediate from **6** maintains a desirable economy of intermediates. The remaining ion pair in Scheme I, **5b**, is invoked through the logic that any norbornenyl products obtained from **8** would not likely necessitate unfavorable electronic changes in the initial cation. It is also possible that cationic interconversion may occur more rapidly than migration, thus **5b** is pictured as derivable from **5a** as well as **8a**.

An alternate means of attaining a nortricyclyl-producing ion pair is that of C_3–C_5 hydride shifts on **5a** or **5b**. This would have the net effect of producing **8a** without an actual counterion migration. While this possibility cannot be eliminated on the basis of present evidence, the observation[3b] that the extremely facile C_2–C_6 hydride shifts of the norbornyl cation are completely suppressed by rapid ion pair collapse in isomerizations of *exo*-2-norbornyl thiocyanate, makes the route seem unlikely. Further, intramolecular anionic migration of a similar variety to that proposed has recently been detected by Goering and Degani[12] during acetolyses of *syn*-7-chloro-*exo*-norbornyl *p*-toluenesulfonate. We have therefore chosen to exclude all hydride shifts from the description of the overall pathway.

Also deleted from serious consideration has been the intermediacy of ion pairs such as **10a**, **10b**, and **10c**.



These presumably equilibrating species, with cations of localized charge, were in theory detectable through the formation of **10** and **11**. (**10c** is particularly attractive in this respect.) As neither thiocyanate nor isothiocyanate of this structure was ever noted, though both are stable to reaction conditions, the decision to use delocalized structures in Scheme I seemed to have firmer theoretical basis.[13]

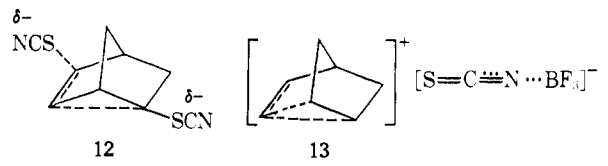
The effects of the ionic catalysts on isomerizations of **6** and **8** were interesting in that the results were dependent on the nature of the anion. In the case of potassium thiocyanate the rates of reaction for both **6** and **8** were slightly accelerated by the presence of the salt, and for the nortricyclyl compound **8** the product ratios were largely unaffected. (A slight shift in favor of norbornenyl products is discernible, but too small to base many assumptions on.) These results, like the more exaggerated but similar effects shown by potassium perchlorate on **6** and **8**, are most easily attributed to the increased ionic strength of the medium. For isomerizations of **6**, the increase in the relative amounts of nortricyclyl thiocyanate (**8**) from potassium thiocyanate catalysis is unique, as it shows the possibility of

(10) This value is derived from the partition of the dehydronorbornyl cation during the treatment of 1-OBs with tetraethylammonium thiocyanate in sulfolane.

(11) If one considers the undetectable S-end reattachment of thiocyanate ion, which can be estimated from the norbornyl studies[3b] to be favored by approximately 2:1 over the observed N attachment, this fraction becomes considerably larger.

(12) H. L. Goering and M. J. Degani, *J. Amer. Chem. Soc.*, 91, 4506 (1969).

(13) No direct evidence has been presented which would exclude the localized nortricyclyl ion, as in **10b**; however the formation of unsaturated products can best be explained by a delocalized ion for the sake of consistency.



12 13

a quasi-displacement reaction (symbolized by **12**) as an alternate pathway to structural interconversion. Of immense aid to this proposal are the results from potassium perchlorate and **6**, which demonstrate that a simple increase in ionizing power of the solvent (the only possible effect of this nonnucleophilic salt) affords larger proportions of *both* nortricyclyl products. In contrast, the displacement process would be expected to favor thiocyanate, as is actually observed, since the nucleophilicity of sulfur end is reported[14] to exceed that of nitrogen end of thiocyanate ion by at least 100-fold in displacement reactions. It is difficult to assess the actual importance of this pathway but it seems surely to result in no more than 15% of the product at the maximum salt concentration employed. Most important, it illustrates that any intermolecular contribution of this type to the product mixtures from the uncatalyzed isomerizations is apt to be negligible, even if the expected minimal ionic separation did not prevail.

Results from boron trifluoride catalyses of the isomerizations of **6** and **8** provided the ultimate end to any thoughts of detecting endo products, and may therefore be the firmest evidence that localized ions in the dehydronorbornyl series are of sufficiently high energy to preclude their existence in ordinary solvents. Since the localized bicyclooctyl cations were demonstrated to best advantage by this technique,[3c] it was assumed that the nonpolar solvent and coordinated counterion would provide the most favorable conditions for detection of the same sort of species derived from **6**. The actual isolation of only a stable mixture of the isothiocyanates **7** and **9** in a nearly identical ratio from **6** and **8** indicates simply that a common intermediate is obtained starting from either thiocyanate. We accordingly represent this coordinated species as **13**.

In summation, it is clear that given sufficiently favorable energy relationships between skeleta, the migration rate of the ions within the alkyl cation–thiocyanate ion pair can exceed the collapse rate. The latter rate is still sufficiently high in the 5-norbornenyl case to cause isolation of an appreciable amount of the thermodynamically less-favored skeleton. Despite this evidence for rapid trapping of the positive ion, no localized carbonium ions were detected. We feel this is a strong argument in favor of the notion that these dehydronorbornyl ions, like the previously examined norbornyl ions, are best represented as delocalized.

Experimental Section[15]

***exo*-Bicyclo[2.2.1]hept-2-en-5-yl Thiocyanate (6).** A mixture of 5.043 g (15.3 mmol) of *endo*-bicyclo[2.2.1]hept-2-en-5-yl *p*-bromobenzenesulfonate and 3.062 g (16.3 mmol) of tetraethylammonium thiocyanate in 40 ml of dry acetone was sealed in a glass tube, and heated on a steam bath for 67 hr. The white precipitate formed during the reaction was removed by filtration and washed three times with 25-ml portions of acetone. The combined filtrate and washings were poured into 200 ml of water and extracted three times with 50 ml of pentane. The combined pentane extracts were washed twice with 50 ml of water and dried. Evaporation of the solvent afforded 2.254 g of a yellow liquid. The crude material, shown by gc to be a mixture of **6**, **7**, **8**, and **9** was separated by chromatography on silica gel. A 0.885-g (40%) sample of the desired compound **6** was collected by preparative gc and distilled at 62.0–63.0° (0.9 mm): infrared spectrum (film) 3010, 2950, 2830, 2150, 727, and 685 cm^{-1}; nmr (CCl_4) τ 4.23 (quad), 7.10 (mult), 8.45 (mult).

Anal. Calcd for C_8H_9NS: C, 63.53; H, 6.00; N, 9.26. Found: C, 63.60; H, 5.90; N, 9.06.

***exo*-Bicyclo[2.2.1]hept-2-en-5-yl Isothiocyanate (7) and *endo*-Bicyclo[2.2.1]hept-2-en-5-yl Isothiocyanate (11).** To a stirred suspension of 20.8 g (0.1 mol) of *N,N'*-dicyclohexylcarbodiimide (DCC) and 45 ml of carbon disulfide in 100 ml of anhydrous ethyl ether was added an ether solution of 10.8 g (0.1 mol) of a mixture of *exo*- and *endo*-bicyclo[2.2.1]hept-2-en-5-yl amines,[6] dropwise at −10°. The mixture was stirred and allowed to rise to room temperature over a period of 3 hr. Stirring was continued for 22 hr, the mixture was filtered, and the residue was washed with ether. The filtrate and washings were combined and concentrated affording 17.029 g of a yellow liquid. This crude material, shown by gc to be a 70:30 mixture of the endo and exo isomers, respectively, was separated by preparative gc. The pure exo isomer **7** was distilled at 63–64° (1.4 mm): infrared spectrum (film) 3030, 2980, 2850, 2100, 858, 794, 773, 724, and 684 cm^{-1}; nmr (CCl_4) τ 4.28 (d quad), 6.71 (tr), 7.13 (mult), 8.42 (quad). *Anal.* Calcd for C_8H_9NS: C, 63.53; H, 6.00; N, 9.26. Found: C, 63.32; H, 5.98; N, 9.17. The pure endo isomer **11** was distilled at 64–65° (1.2 mm): infrared spectrum (film) 3030, 2980, 2850, 2100, 848, 832, 812, 768, 732, and 686 cm^{-1}; nmr (CCl_4) τ 3.70 (d quad), 5.87 (d tr), 6.78 (br s), 7.03 (br s), 7.80 (hept), 8.69 (mult). *Anal.* Calcd for C_8H_9NS: C, 63.53; H, 6.00; N, 9.26. Found: C, 63.60; H, 6.02; N, 9.24.

1-[*exo*-Bicyclo[2.2.1]hept-2-en-5-yl]-3-*tert*-butylthiourea. The derivative of **7** was prepared by a previously described technique[3a] affording white needles: mp 162.5–163.0°; infrared spectrum (KCl pellet) 3395, 3275, 2950, 1535, 1330, 990, 960, 710, and 692 cm^{-1}.

Anal. Calcd for $C_{12}H_{20}N_2S$: C, 64.24; H, 8.98; N, 12.49. Found: C, 64.42; H, 9.09; N, 12.54.

1-[*endo*-Bicyclo[2.2.1]hept-2-en-5-yl]-3-*tert*-butylthiourea. The derivative of **11** was prepared as before[3a] affording white needles: mp 166–166.2°; infrared spectrum (KCl pellet) 3395, 3275, 2950, 1535, 1330, 996, 832, 722, and 692 cm^{-1}.

Anal. Calcd for $C_{12}H_{20}N_2S$: C, 64.24; H, 8.98; N, 12.49. Found: C, 64.37; H, 8.90; N, 12.42.

***endo*-Bicyclo[2.2.1]hept-2-en-5-yl Thiocyanate (10).** A solution of 5.395 g (43.1 mmol) of a mixture of the endo and exo thiols[3a] in 4.36 g (43.1 mmol) of triethylamine was added dropwise, with stirring, to a solution of 3.0 g (49 mmol) of cyanogen chloride in 100 ml of dry ether. The solution was stirred for 24 hr and washed twice with 50 ml of water, twice with 50 ml of saturated sodium bicarbonate, and twice more with water. The ether solution was dried and concentrated. Distillation of the residue gave 1.501 g (23.2%) of a colorless liquid: bp 83–80° (3 mm). The distilled material, shown by gc to be a 77:23 mixture of the *endo*- and *exo*-thiocyanates, was further purified by preparative gc. An analytical sample of the pure endo isomer **10** was distilled at 69–70° (1.3 mm): infrared spectrum (film) 3010, 2950, 2830, 2150, 729, and 692 cm^{-1}; nmr (CCl_4) τ 3.70 (oct), 6.07 (tr), 6.20 (tr), 6.70 (br s), 6.98 (br s), 7.68 (hept), 8.55 (mult), 8.97 (tr), 9.18 (tr).

Anal. Calcd for C_8H_9NS: C, 63.53; H, 6.00; N, 9.26. Found: C, 63.62; H, 6.26; N, 9.04.

Tricyclo[2.2.1.$0^{2,6}$]hept-3-yl Thiocyanate (8). To 13.530 g (41 mmol) of crude *p*-bromobenzenesulfonate ester, prepared from 3-

(14) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Amer. Chem. Soc.*, 87, 1045 (1965).

(15) Melting points and boiling points were uncorrected. Infrared spectra were obtained on a Perkin-Elmer Infrared Model 137B using sodium chloride optics. Nmr spectra were obtained using a Varian Associates A60A spectrometer. An F&M gas chromatograph was employed for collection of pure samples, for analyses of isomerization mixtures, and for kinetic measurements. Packing materials were 15% diethylene glycol succinate on 60–80 mesh Chromosorb W, 15% tetracyanoethylpentaerythritol on 60–80 mesh Chromosorb P, and 20% butanediol succinate on 60–80 mesh Chromosorb W. Organic solvents were of ACS Reagent Grade unless otherwise stated. Sulfolane was treated with potassium permanganate and distilled under vacuum. Dimethylformamide was distilled from calcium hydride, and methyl ethyl ketone was distilled from potassium carbonate and potassium permanganate. Elemental analyses were carried out by Micro-Analysis, Inc., of Wilmington, Del.

hydroxynortricyclene,[16] was added 8.498 g (45 mmol) of tetraethylammonium thiocyanate dissolved in 100 ml of freshly distilled dry sulfolane. The mixture was heated at 100° for 28 hr and the reaction mixture poured into 350 ml of water and extracted three times with pentane. The combined extracts were washed twice with water, dried, and concentrated. The crude material, shown by gc to be contaminated with isothiocyanates, was purified as described for **6**. The pure thiocyanate **8** was ultimately obtained in 68% yield and distilled at 72–73° (1.1 mm): infrared spectrum (film) 3010, 2925, 2840, 810, 764, and 728 cm^{-1}; nmr (CCl_4) τ 6.72 (s), 7.88 (s), 8.28 (s), 8.58 (s), 8.71 (s).

Anal. Calcd for C_8H_9NS: C, 63.53; H, 6.00; H, 9.26. Found: C, 63.64; H, 6.06; N, 9.03.

Tricyclo[2.2.1.0^{2,6}]hept-3-yl Isothiocyanate (9). The isothiocyanate was prepared in the same manner as described for **7** and **11** using 2.680 g (13 mmol) of DCC, 9.885 g (130 mmol) of carbon disulfide in 50 ml of anhydrous ether, and an ether solution of 1.418 g (13 mmol) of 3-aminonortricyclene.[17] This procedure afforded a 38% yield of crude material, shown by gc to be contaminated with azide which was used to prepare the amine. The desired product, **9**, was collected by preparative gc and a sample distilled at 65–66° (1.2 mm): infrared spectrum (film) 3030, 2890, 2850, 2100, 908, 882, 810, 790, 758, and 680 cm^{-1}; nmr (CCl_4) τ 6.38 (s), 7.81 (s), 7.98 (s), 8.17 (s), 8.47 (s), 8.61 (s).

Anal. Calcd for C_8H_9NS: C, 63.53; H, 6.00; N, 9.26. Found: C, 63.67; H, 6.00; N, 9.26.

1-[Tricyclo[2.2.1.0^{2,6}]hept-3-yl]-3-*tert*-butylthiourea. The derivative of **9** was prepared as before[3a] affording white needles: mp 172.9–173.2°; infrared spectrum (KCl/pellet) 3395, 3275, 2950, 1535, 1330, 813, 795, 709, and 692 cm^{-1}.

Anal. Calcd for $C_{12}H_{20}N_2S$: C, 64.24; H, 8.98; N, 12.49. Found: C, 64.52; H, 9.04; H, 12.75.

Product Studies. Solutions 0.17, 0.017, or 1.7 *M* in pure alkyl thiocyanate or isothiocyanate were prepared using sulfolane, acetonitrile, dimethylformamide, methyl ethyl ketone, or diglyme. One-milliliter aliquots were sealed in glass tubes under a nitrogen atmosphere and heated at 150° for various time intervals. Quenching by cooling was followed by pouring the contents of the tubes into 25 ml of water, and extraction with two 5-ml portions of pentane. The combined extracts were washed twice with water, dried, and concentrated. Material recovery was always in excess of 96% (crude), thus the residues were examined directly by gc using the following columns and conditions: (1) column, 12 × 1/4 in. diethylene glycol succinate; temp, 150°; carrier flow, 60 ml/min; R_t (min), **7**, 6.8; **11**, 7.4; **9**, 9.1; **6**, 10.8; **10**, 11.8; **8**, 14.3; (2) column, 6 × 1/8 in. tetracyanoethyl pentaerythritol; temp, 150°; carrier flow, 47 ml/min; R_t (min) **7**, 4.5; **11**, 5.4; **9**, 6.1; **6**, 8.4; **10**, 9.8; **8**, 11.2; (3) column, 8 × 1/4 in. butanediol succinate; temp 180°; carrier flow, 60 ml/min; R_t (min) **7**, 8.6; **11**, 9.8; **9**, 10.8; **6**, 12.4; **10**, 14.2; **8**, 16.1.

Product Studies with Salt Catalysis. One-milliliter aliquots of sulfolane solutions which were 0.1 or 0.01 *M* in potassium thiocyanate or potassium perchlorate and 0.17 *M* in alkyl thiocyanate were sealed in glass ampoules and treated as described above. Analytical conditions were identical with those of the uncatalyzed runs.

Product Studies with Boron Trifluoride Catalysis. To 10 ml of a 0.3 *M* solution of boron trifluoride in benzene was added enough alkyl thiocyanate to bring its concentration to 0.17 *M*. This mixture was heated at reflux and 1-ml aliquots removed at various time intervals. The samples were mixed with 5-ml portions of pentane, washed with a saturated solution of sodium bicarbonate, and dried. After concentration the residues were analyzed as described above.

Kinetic Procedure. One-milliliter or 0.5-ml aliquots of 0.04 *M* sulfolane solutions of alkyl thiocyanate were sealed in glass ampoules under a nitrogen atmosphere and heated at 130.0 or 150.0°. Tubes were removed at intervals and quenched by immersion in ice. Isolations of the products were accomplished as for previously described product studies, as were gc analyses of the rate of starting thiocyanate disappearance.

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(16) J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, 72, 3116 (1950).

(17) The amine was prepared from 3-bromonortricyclene[16] by tetramethylguanidinium azide displacement[3d] followed by lithium aluminum hydride reduction of the crude nortricyclyl azide.