The Nature of the Carbonium Ion. V. The Bicyclooctyl Cations from Thiocyanate Isomerizations[1a]

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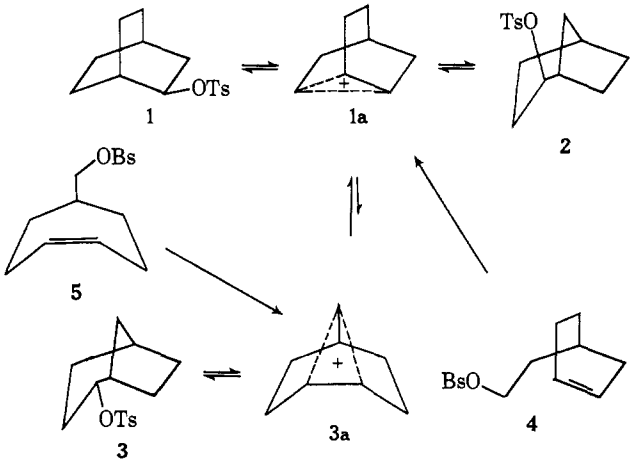
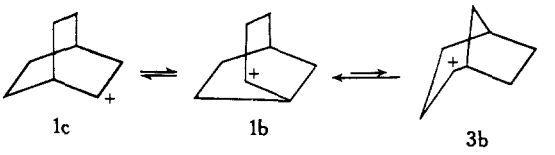
Abstract: The π-route and σ-route carbonium ions of the bicyclo[2.2.2]oct-2-yl–*exo*-bicyclo[3.2.1]oct-2-yl series were studied using the thiocyanate isomerization technique for trapping carbonium ions. Isomerizations of 2-(Δ^3-cyclohexenyl)ethyl (**9**), bicyclo[2.2.2]oct-2-yl (**11**), and *exo*-bicyclo[3.2.1]oct-2-yl (**13**) thiocyanates were conducted in several aprotic solvents. Under most conditions, irrespective of the starting thiocyanate, product mixtures were obtained in which almost equal amounts of the [2.2.2]- and *exo*-[3.2.1]isothiocyanates (**12** and **14**) occurred. The remaining products tended to be quite dependent on the original position of the counterion in the ion pair, as was observed through solvent, catalyst, and temperature studies. 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. The appearance of *endo*-bicyclo[3.2.1]oct-2-yl thiocyanate (**18**) in several product mixtures revealed a major subsequent difference between the isomerization and solvolysis intermediates. A comprehensive interpretation of the results is proposed involving ions of localized and delocalized charge.

As homologs of the much investigated[2] norbornyl cations, the bicyclooctyl cations obtained from solvolyses or deaminations of various bicyclo[2.2.2]-octyl, bicyclo[3.2 1]octyl, and related derivatives have received a fair amount of characterization.[2,3] In a recent thorough study of the processes occurring subsequent to ionization of bicyclo[2.2.2]oct-2-yl and bicyclo-[3.2.1]oct-2-yl arylsulfonates, Goering and Fickes[3a] were able to establish the necessity for both "classical" (localized charge) and "nonclassical" (delocalized charge) intermediates during solvolysis. In general, they concluded that while the initial ionizations of bicyclo[2.2.2]oct-2-yl *p*-toluenesulfonate (**1**), *exo*-bicyclo-[3.2.1]oct-2-yl *p*-toluenesulfonate (**2**), and *endo*-bicyclo-[3.2.1]oct-2-yl *p*-toluenesulfonate (**3**) lead almost completely to nonclassical ions **1a** (from **1** and **2**) or **3a**



(from **3**), there is ample reason to suspect some subsequent "leakage" of these ions to the classical counterparts, **1b**, **1c**, and **3b**. This argument, which was based



primarily on studies of optically active **1**, **2**, and **3**, is in accord with the observations of Berson, *et al.*,[3b] on the cations obtained from 2- and 7-norbornylcarbinyl derivatives. The cationic intermediates from solvolysis of 2-(Δ^3-cyclohexenyl)ethyl *p*-bromobenzenesulfonate[4] (**4**), while not examined by these authors, should also be included in this description if the logic[3a] applied to those from its Δ^4-cycloheptenylmethyl (**5**) isomer[5] is adopted. Despite the seeming interrelationships of these ions, the product ratios from solvolysis depend in most cases on the arylsulfonate source. Product distributions from **1**, **2**, and **4** (which are nearly identical) are quite unlike those from **3** and **5** (also very similar). This fact is easily attributable to the initial formation of ions like **1a** in the former cases as compared with **3a** from the latter. An inconsistency in this explanation was presented by the report that the optical properties of the products from resolved **1** and **2** were nonidentical. This subtle observation was difficult to accommodate only with **1a** and created the necessity for **1b** and **1c**.[3c] Particularly interesting was the report that even at the ion pair stage, nonclassical–classical leakage occurred. It was nevertheless uncertain whether this was due to real ion interconversions or to some unassisted ionization accompanying the major assisted process.

As this matter seemed worth further exploration, primarily in the area of ion pair behavior, we became interested in the application of the thiocyanate–isothiocyanate thermal isomerzation technique[6] to these cations.

(1) (a) Presented in part at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, Abstracts, S-4; (b) address correspondence to this author at Brown University; (c) Brown University.

(2) See J. A. Berson in "Molecular Rearrangements," Vol. I, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3.

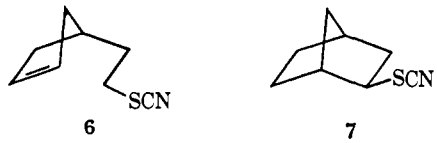
(3) (a) H. L. Goering and G. N. Fickes, *J. Amer. Chem. Soc.*, 90, 2848, 2856, 2862 (1968); (b) J. A. Berson and P. Reynolds-Warnhoff, *ibid.*, 86, 595 (1964); J. A. Berson and D. Willner, *ibid.*, 86, 609 (1964); J. A. Berson and M. S. Poonian, *ibid.*, 88, 170 (1966); (c) H. L. Goering and M. F. Sloan, *ibid.*, 83, 1992 (1961).

(4) S. Winstein and P. Carter, *ibid.*, 83, 4485 (1961).

(5) G. LeNy, *C. R. Acad. Sci., Paris*, 251, 1526 (1960).

(6) 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., 1969; A. Fava in "The Chemistry of Organic Sulfur Compounds," Vol. 2, N.

In two previous papers of this series we have described similar studies of the π-route norbornyl cation from 2-(Δ^3-cyclopentenyl)ethyl thiocyanate (**6**)[7] and the σ-route norbornyl cation from *exo*-2-norbornyl thiocyanate (**7**).[8] In both instances the behavior of ion pairs was



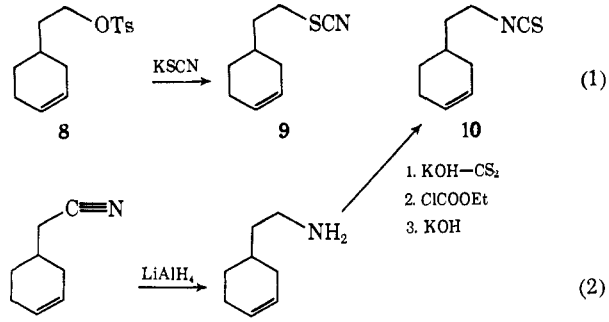
6 **7**

detectable because of a reluctance of these species to undergo further dissociation. No evidence was seen in either case for classical ions, even though ion pair collapse was sufficiently rapid to completely preclude hydride shifts. Most importantly, the discovery that unassisted ionization is impossible for primary and secondary thiocyanates ruled out dual ionization pathways as a complication in the analysis of our results. We have therefore chosen to synthesize the thiocyanate analogs of **1**, **2**, **3**, and **4** for purposes of study.

Results

The *p*-toluenesulfonate ester (**8**) of 2-(Δ^3-cyclohexenyl)ethanol[4] was used as the precursor of 2-(Δ^3-cyclohexenyl)ethyl thiocyanate (**9**). The reaction of **8** with potassium thiocyanate in sulfolane gave a mixture of **9** and its isomeric isothiocyanate **10** in a 90:10 ratio (Scheme I, eq 1). Preferential reaction of **10** with *n*-butylamine afforded pure **9** after distillation. 2-(Δ^3-Cyclohexenyl)ethyl isothiocyanate (**10**) was prepared independently by the reaction of carbon disulfide, ethyl chloroformate, and potassium hydroxide with the corresponding amine (eq 2).

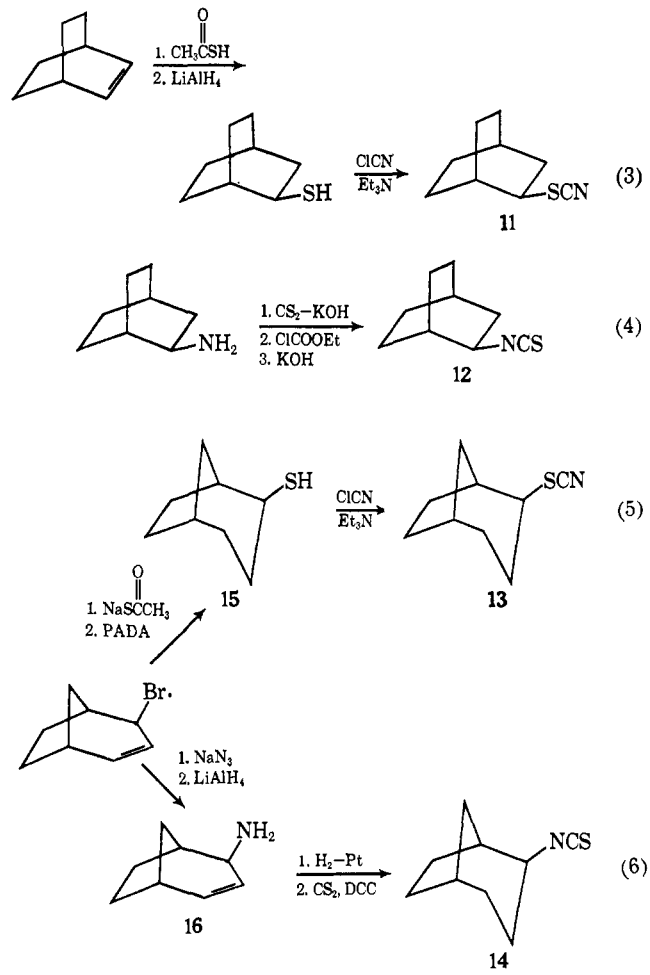
Scheme I



As displacements by thiocyanate ion on either **1** or **3** gave inseparable complex mixtures of bicyclic thiocyanates and isothiocyanates, an individual synthesis of each bicyclic compound had to be devised in order to ensure structural homogeneity. Treatment of bicyclo[2.2.2]oct-2-yl thiol with cyanogen chloride afforded pure bicyclo[2.2.2]oct-2-yl thiocyanate (**11**) (Scheme II, eq 3).

Use of the previously described method (eq 4) gave bicyclo[2.2.2]oct-2-yl isothiocyanate (**12**) from the corresponding amine.[9] Authentic samples of *exo*-bicyclo[3.2.1]oct-2-yl thiocyanate (**13**) and isothiocyanate (**14**) were prepared from *exo*-bicyclo[3.2.1]oct-3-en-2-yl bro-

Scheme II



mide.[9] Substitution on this bromide by sodium thiolacetate (eq 5), followed by simultaneous diimide reduction of the double bond, and ester cleavage gave *exo*-bicyclo[3.2.1]octane-2-thiol (**15**), whose treatment with cyanogen chloride afforded isomerically pure **13** (eq 5). Sodium azide reaction with the bromide (eq 6) followed by lithium aluminum hydride reduction gave *exo*-bicyclo[3.2.1]oct-3-en-2-yl amine (**16**) which was catalytically hydrogenated after conversion to its benzoate salt. The resultant saturated amine was then allowed to react with carbon disulfide and N,N′-dicyclohexylcarbodiimide to give pure **14** (eq 6). In preparation of the *endo*-thiocyanate **18**, a conventional reduction–arylsulfonate esterification–displacement sequence converted Δ^4-cycloheptene carboxaldehyde[9] to Δ^4-cycloheptenylcarbinyl thiocyanate (**17**). Isomerization of **17** in sulfolane afforded the following mixture: 9% **19**; 52% Δ^4-cycloheptenylcarbinyl isothiocyanate; 37% **18**; and 2% unreacted starting material. Chromatography on silica gel separated thiocyanates from isothiocyanates. A subsequent treatment of the combined thiocyanate fractions with a solution of bromine on carbon tetrachloride gave, after distillation, pure *endo*-bicyclo[3.2.1]oct-2-yl thiocyanate (**18**) (Scheme III, eq 7).

endo-Bicyclo[3.2.1]oct-2-yl isothiocyanate (**19**) was prepared from the corresponding amine[9] by the method previously described (eq 8). Infrared and nmr spectra (see Experimental Section) for all compounds were in accord with the structural assignments, and minimum

Kharasch and C. Y. Meyers, Ed., Pergamon Press, Oxford, England, p 73.

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

(8) L. A. Spurlock and T. E. Parks, *ibid.*, **92**, 1279 (1970).

(9) See Experimental Section.

Table I. Isomerizations of 0.15 *M* Solutions of 9

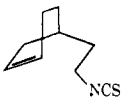
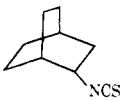
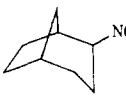
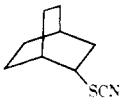
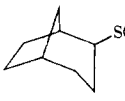
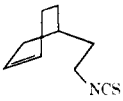
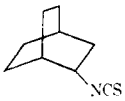
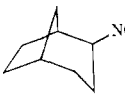
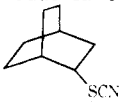
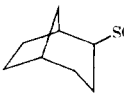
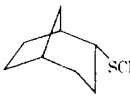
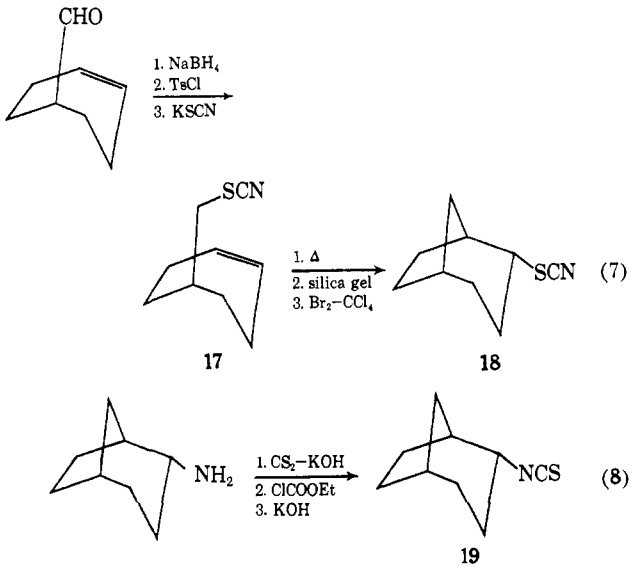
Solvent	Time, hr	Temp, °C	% isomerzn	Relative product ratio					10/(12 + 14)
									
Sulfolane	24	150.0	6	48	19	12	5	16	1.5
	48		11	43	23	14	5	15	1.2
	24	165.0	13	46	28	15	3	8	1.06
	48		26	44	34	18	2	2	0.85
	12	175.0	13	39	36	18	3	4	0.74
CH_3CN	24	150.0	1	71	9	8	3	9	4.2
	48		3	61	17	9	3	10	2.3
MEK	24		2	89	2	6	2	1	11.1
	48		3	90	2	5	1	2	12.8

Table II. Catalyzed Isomerizations of 0.15 *M* Solutions of 9

Solvent	Catalyst (concn)	Time, hr	Temp, °C	% isomerzn	Relative product ratio					
										
Sulfolane	KSCN (0.1 *M*)	24	150.0	43	93	2	1	1	3	
CH_3CN				16	96	1	1	1	1	
MEK				31	>99	Tr	Tr	Tr	Tr	
Benzene	BF_3 (2%)	24	80	21	31					69
		48		26	29					71
		72		30	29					71

purity in excess of 99.5% could be confirmed by gc and elemental analyses.

Scheme III



The isomerizations of thiocyanates **9**, **11**, and **13** were conducted in a variety of aprotic solvents at several temperatures. Products of the reactions were examined by gc and their identities confirmed by comparison of their retention times with those of authentic materials. The values listed are the averaged of at least two runs, with overall material recovery 90–95%. Table I summarizes the results of solvent influence on the relative product ratios and on the extent of isomerization of thiocyanate **9**. Observation indicated the product ratios to be characteristic of solvent, temperature, and time. The most reliable results were obtained in sulfolane, where less decomposition and more rapid isomerizations occurred. The variation with temperature of the product ratio **10**/(**12** + **14**) probably reflects the sensitivity of the cyclization mechanism to the energy available in the medium. In this fashion, the barrier between the ions leading to **10** and to **12** or **14** is discernible. Unfortunately, this observation is complicated by decomposition effects[10] and the concurrent isomerizations of **11** and **13**. (As will be shown later these cyclized thiocyanates give their corresponding isothiocyanates at rates greater than six times the isomerization rate of **9**.) The effect of solvent polarity, observable as an increase in the ratio **10**/(**12** + **14**) upon changing from sulfolane to acetonitrile to methyl ethyl ketone, is probably connected to the position of the thiocyanate ion

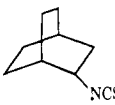
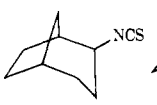
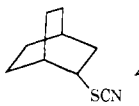
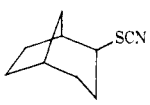
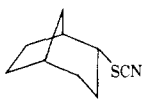
$$S^{\delta-}\cdots C\equiv N^{\delta-}$$

with respect to the faces of the cation. The most polar solvent, sulfolane, allows for the greatest mobility of the two ion pair components relative to each other, and thus the largest proportions of cyclized products (which *a priori* must result from ions other than the initially obtained pairs) were obtained from this medium.

Table II shows the effects of catalysts on the isomerizations of **9**. Solutions 0.15 *M* in thiocyanate **9** and 0.1 *M* in potassium thiocyanate were allowed to react under the same conditions as the uncatalyzed isomerizations. Of interest is the rate enhancement which occurs with the added salt. The nearly exclusive formation of uncyclized product **10** almost assuredly arises through a

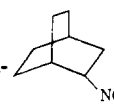
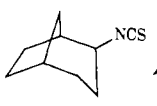
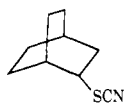
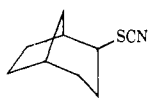
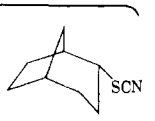
(10) Control experiments indicated that uncyclized isothiocyanate, **10**, decomposes slowly with increasing temperature and length of reaction, thus implicating this process as contributing to the decrease in the **10**/(**12** + **14**) ratio with increasing reaction temperature.

Table III. Isomerizations of 0.15 *M* Solutions of **11** and **13**[a]

RSCN	Solvent	Temp, °C	% isomerzn	Relative product ratio: 				
11	Sulfolane	130.5	29	15	11		74	
13			13	23	14	63		
11		150.0	48	48	34		14	4
13			42	43	31	19		7
11		165.0	75	56	35		6	3
13			68	50	34	6		10
11	CH_3CN	150.0	9	25	18		57	
13			16	30	19	51		
11	DMF		20	30	26		44	
13			18	28	21	44		7

[a] Reaction time was 24 hr except at 165.0° where the values given are for 12 hr.

Table IV. Catalyzed Isomerizations of 0.15 *M* Solutions of **11** and **13**

RSCN	Solvent	Catalyst (concn)	Time, hr	Temp, °C	% isomerzn	Relative product ratio: 				
11	Sulfolane	KSCN (0.1 *M*)	24	150	58	53	30		10	7
13					56	44	29	10		17
11	CH_3CN				17	44	28		28	
13					20	33	21	39		7
11	Benzene	BF_3 (2%)		80	90	54	41		1	4
13					66	51	33	8		8
13				25	10	28	19	6		47

bimolecular displacement by thiocyanate ion on the primary thiocyanate rather than through any salt effect on the dissociation process. Prior observations have shown this to be the case with the isomerizations of the homologous 2-(Δ^3-cyclopentenyl)ethyl thiocyanate (**6**), and there seems no reason to suppose otherwise in this case.[7]

Heating solutions of **9** at reflux in benzene which was 2% in boron trifluoride afforded the results of Lewis acid catalysis shown in Table II. The influence of this catalyst is quite striking since we were unable to obtain isomerization in benzene at any temperature up to 150° without catalysis.

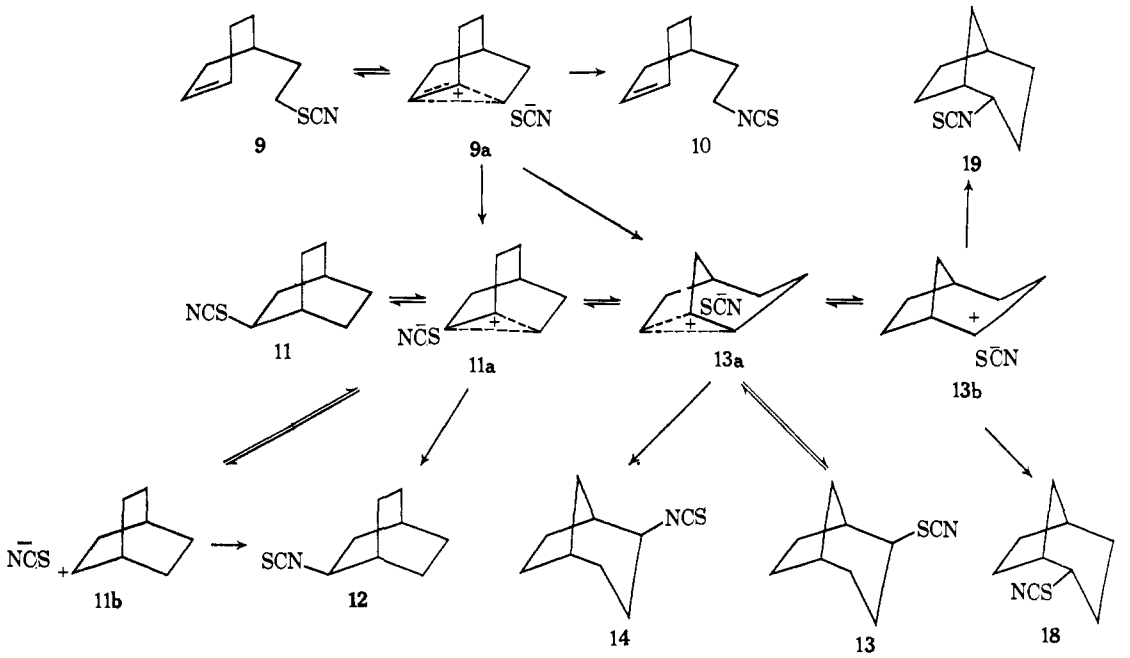
The results from studies of solvent and temperature influences on the relative product ratios and on isomerization rates of cyclized thiocyanates **11** and **13** are tabulated in Table III. As in the prior case, the best results were obtained in sulfolane. A striking result occurred in the detection of significant amounts of *endo*-bicyclo[3.2.1]oct-2-yl thiocyanate (**18**) during isomerizations of **11** and **13**. The presence of the isomeric isothiocyanate **19** could not, however, be determined due to its inseparability from isothiocyanate **12** under all conditions which we employed. Owing to the prevalence of sulfur-end attack over nitrogen attack for thiocyanate ion on most carbonium ions,[11] it is likely that the relative proportion of **19** in all of the product mixtures was quite small.

Table IV shows the results of catalytic effects on the isomerization of thiocyanates **11** and **13**. In nearly every case an appearance of **18** in the product mixture again leaves suspect the additional presence of isothiocyanate **19**. Even more than in the uncatalyzed isomerizations, however, the relative amounts of this compound are expected to be small. Displacement processes with thiocyanate ion are well documented[11] to proceed heavily through sulfur attack, and the boron trifluoride–thiocyanate complex shows a similar preference in its collapse on cations. The amounts of thiocyanate **18** formed therefore probably indicate the total extent of *endo* products. The increased proportions of **18** from the potassium thiocyanate catalyzed isomerizations of **11** and **13** presumably result from simple displacements on **13**. It follows that the only small rate increases and slight changes in product distribution demonstrate the decreased importance of direct substitution of this secondary thiocyanate, as compared with substitution at the primary carbon of **9**. Displacement on **11**, undetectable in its prevalent sulfur-end form, is somewhat apparent in the small increase of retained-structure isothiocyanate **12** relative to **14**. The comparative unimportance of nitrogen-end attack by thiocyanate ion renders this observation of minimal utility in estimating the relative susceptibilities of **11** and **13** to direct displacements.

Table V shows the first-order rate constants for the isomerizations of **9**, **11**, and **13**. Rate measurements in solvents other than sulfolane were not effected due to the aforementioned undesirable secondary processes occurring in most media. The isomerizations of all three compounds were followed by gc. Graphs (log [RSCN] *vs. t*) of the data from the bicyclic thiocyanates **11** and **13** showed linearity to a minimum of 20% reaction, while uncyclized thiocyanate **9** exhibited linear first-order be-

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

Scheme IV



havior only to approximately 4% reaction at 165.0°. (The accompanying formation and isomerization of the more reactive thiocyanates **11** and **13** as well as decomposition of isothiocyanate **10** tended to obscure the results from **9** past this small per cent isomerization.) The ratio of rates observed for the bicyclic thiocyanates at both temperatures (k_{11}/k_{13} = 1.8) is arresting in its resemblance to the solvolytic rate ratio (k_1/k_2 = 1.7)[3c] for the analogous *p*-toluenesulfonates, **1** and **2**. In addition, the much slower rate recorded for the unsaturated isomer **9** is in accord with the slow solvolytic rate of **4** (though perhaps not so pronounced). When coupled with the calculated values for the activation parameters, which are quite typical of previously examined thiocyanates,[7,8] the rate relationships provide the ultimate confirmation that the initial process in isomerizations of **9**, **11**, and **13** is unimolecular ionization.

Table V. Rate Data for Isomerizations of **9**, **11**, and **13** in Sulfolane

RSCN	Temp, °C	$k \times 10^7$, sec^{-1}	$t_{1/2}$, hr	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
11	130.0	7.7 ± 0.03	249.9	30.1	−12.5
	150.0	45.9 ± 0.5	41.9		
13	130.0	4.2 ± 0.04	461.2	30.5	−12.7
	150.0	25.2 ± 0.6	76.3		
9	165.0	6.2 ± 0.06	312.3		

Discussion

Owing to the nearly identical product distributions obtained from the solvolyses of the arylsulfonate esters **1**, **2**, and **4**, it has been concluded[3a] that these compounds give the same product-forming intermediate. Table VI gives a comparison of the [2.2.2] and *exo*-[3.2.1] isomers obtained from solvolyses and isomerizations. The resemblance of these values indicates that both solvolysis and isomerization proceed through similar intermediate species. In solvolysis the major intermediate is **1a**. For isomerizations, it is nevertheless necessary to invoke at least two such intermediates, **11a** and **13a** (Scheme IV), since the overall product distributions from the [2.2.2]thiocyanate **11**, and the *exo*-[3.2.1]thiocyanate **13**, are nonidentical under most conditions. This can be explained best as the result of differences in counterion position in the initial ion pairs. The assumption is made that thiocyanate ion will reside closer to its original site of detachment in the first formed ion pair from each thiocyanate. The two pairs, **11a** and **13a**, therefore possess the same cationic structure, while differing only in counterion location. To these rapidly equilibrating species is attributed the role of principal product forming intermediates from **11** and **13**.

Table VI. Ratios of Isomers Obtained from Isomerizations of **9**, **11**, and **13** Compared with the Solvolyses of **1**, **2**, and **4**

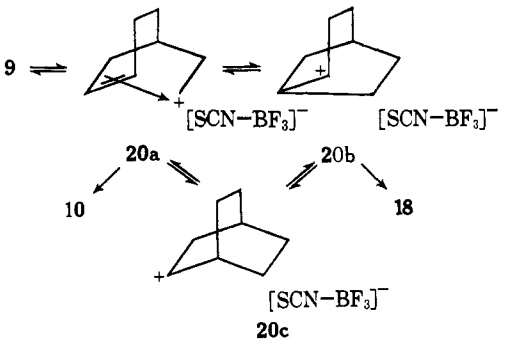
Compd	Solvent	% [2.2.2]	% *exo*-[3.2.1]
4[a]	HOAc	54	46
9[b]	Sulfolane	61	39
	CH_3CN	53	47
1[c]	HOAc	54	46
11[b]	Sulfolane	58	42
	CH_3CN	58	42
	DMF	54	46
2[c]	HOAc	54	46
13[b]	Sulfolane	58	42
	CH_3CN	61	39
	DMF	57	43

[a] Reference 4. [b] Values are of isothiocyanates **12** and **14** produced at 150° for 24 hr. [c] Reference 3a.

An adequate explanation of the isomerization products from the unsaturated thiocyanate **9** likewise requires a consideration of the counterion. The bicyclic products, **11**, **12**, **13**, and **14**, are most consistently seen as derived from the **11a** ⇌ **13a** equilibrating pairs. The major product, unsaturated isothiocyanate **10**, must be obtained from an ion pair resembling **9a**. "Unassisted"

(solvent assisted) ionization of the primary thiocyanate **9** could be ruled out from previous work.[7,12] (This is conveniently different from the corresponding solvolysis of *p*-bromobenzenesulfonate **4** where the small amounts of uncyclized products probably result from solvent assistance to ionization.) Additional information concerning **9a** was deduced from the failure of the bicyclic thiocyanates, **11** and **13**, to produce detectable amounts of isothiocyanate **10**. This indicated that the counterion migration which converts **9a** to **11a** or **13a** must be essentially irreversible. The alternate representation of the initial species from **9**, an equilibrating set of ion pairs with localized cations, cannot be differentiated from **9a** using sulfolane as solvent. We prefer the delocalized structure for simplicity.

In less polar solvents it is conceivable that more localized charge structures become necessary for cation stability. Most persuasive support for this assumption comes from the boron trifluoride catalysis results obtained in the nonpolar solvent, benzene (Table II). In this case the isolation of **10** and the *endo*-[3.2.1]thiocyanate **18**, as the only products, is quite easily rationalized through the equilibrating localized structures **20a** and **20b**. (The isomeric **20c** is included for consistency.)

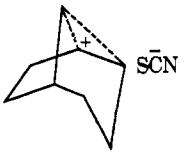


20c

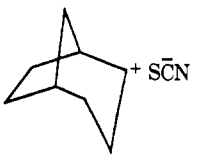
These ions appear most attractive as intermediates since they require a minimum of counterion migration in order to give the observed products.

A similar case can be made for the boron trifluoride results from **11** and **13** (Table IV). The pronounced temperature effect shown by the *exo*-[3.2.1]thiocyanate **13** is particularly revealing with respect to the intervention of cations with localized charge. The large proportions of *endo*-[3.2.1]thiocyanate **18** in the products from the room temperature runs seemingly result from the collapse of ion pairs in which anionic migration, being limited by the poorly solvating medium, involves only an exchange of faces with respect to the cation at C_2. At higher temperatures this effect is much less discernible due to the greater energy available to the ion pair and the resultant increase in migratory ability of the counterion.

The detection of significant amounts of *endo*-[3.2.1] product **18** from the isomerization of **11** and **13** in sulfolane is perhaps more important since it demonstrates that localized cations are formed even in a polar solvent. This attack by the nucleophile on the *endo*-face of C_2 has no correspondence in the results obtained from acetolyses of the related arylsulfonate esters, **1** and **2**. For acetolysis, according to Goering and Fickes,[3a] the activation energy for leakage and capture of the ions directly related to **1** and **2** (**1a, b**) is 2 kcal/mol higher than that for ions related to the *endo*-[3.2.1] isomer **3** (**3a, b**). If the energy of capture is about the same for all of these ions (a seemingly reasonable supposition), the activation energy difference must be due to the greater stability of ions **1a, b**. It is assumed that this is the reason for the existence of system crossover in only one direction (**3b** → **1b**) during acetolyses. In our case the activation energy for capture should be even lower than in acetic acid due to the intimacy of the ion pairs and the great nucleophilicity of the thiocyanate ion. We would expect, therefore, that the barrier to leakage (**1b** → **3b**) would be even more pronounced in these thermal isomerizations than in the solvolytic reactions. Finding that product distributions do *not* support this, in that *endo*-[3.2.1] product is actually isolated, requires an explanation which nonetheless involves no crossover from ions resembling **1a, b** to those resembling **3a, b**. Assuming the same ion relationships in solvolyses and isomerizations, the *endo* product cannot be derived from either the delocalized cation **18a** or the localized chair cation **18b**. It must arise rather from attack on the localized boat cation (**13b**)[13] obtained directly from the delocalized intermediate **13a**. In this manner the presence of *endo*-[3.2.1] product can be reconciled with the expected rapid attack on the cation by thiocyanate ion, and the improbability[14] of unassisted ionization.



18a



18b

We have not included a consideration of hydride shifts in the overall reaction sequence for two reasons. (1) It has been observed[8] that there are no hydride shifts detectable during isomerizations of *exo*-2-norbornyl thiocyanate (**7**) under conditions identical with those which we have employed and; (2) a recent analysis of 7,2-hydride shifts of the bicyclooctyl cations has indicated them to be decidedly slower than the analogous 6,2-hydride shifts of the norbornyl skeleton.[15] This seems ample reason for their exclusion from Scheme IV.

One indirect feature of this work seems worthy of final mention. The confirmation of the sensitivity of thiocyanate isomerization techniques to cation charge distribution is instructive not only with regard to the bicyclooctyl cations, but to the previously examined[7,8] norbornyl cations as well. The failure, in fact, to detect localized norbornyl ions by this rapid trapping method must be considered strong evidence for the lack of their existence.

Experimental Section

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; approxi-

(12) P. A. S. Smith and D. W. Emerson, *J. Amer. Chem. Soc.*, **82**, 3076 (1960).

(13) This ion admittedly may show a preference for *exo* attack but the possibility of accompanying *endo* attack is enhanced by the previously discussed observation of *endo* product formation during boron trifluoride catalyzed isomerizations of **9**.

(14) Cyclohexyl thiocyanate failed to isomerize after 48 hr at 150° in sulfolane, and 36 hr at 80° in benzene with boron trifluoride. This leaves little doubt of the necessity for assisted ionization and the initial presence of only delocalized ions.

(15) H. Kwart and J. L. Irvine, *J. Amer. Chem. Soc.*, **91**, 5541 (1969).

mately 20% solutions in CCl_4 were employed with tetramethylsilane as the internal standard. Analyses were carried out by Micro-Analysis, Inc. of Wilmington, Del.

2-(Δ^3-Cyclohexenyl)ethyl Thiocyanate (9). A mixture of 15.1 g (0.054 mol) of crude *p*-toluenesulfonate ester prepared from 8.8 g of 2-(Δ^3-cyclohexenyl)ethanol[4] and 5.7 g (0.057 mol) of potassium thiocyanate was dissolved in 60 ml of sulfolane and heated at 75° for 18 hr. The mixture was added to 600 ml of water and extracted with pentane. The extracts were dried and concentrated affording 9.4 g of crude thiocyanate. The crude material, shown by gc to be contaminated with approximately 10% isothiocyanate **10**, was added to 1.53 g (0.021 mol) of *n*-butylamine in 50 ml of dry dioxane and stirred for 18 hr. The mixture was then added to 200 ml of water and extracted with pentane. The combined extracts were washed successively with 10% hydrochloric acid and saturated sodium bicarbonate solution, then dried and concentrated. Distillation of the residue gave 5.77 g (64%) of **9**: bp 85–87° (0.5 mm); infrared spectrum (film) 3020, 2910, 2150, and 650 cm^{-1}; nmr (CCl_4) τ 4.35 (s), 7.02 (tr), 7.55–9.08 (mult).

Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.81; N, 8.38; S, 19.18. Found: C, 64.62; H, 7.64; N, 8.28; S, 19.01.

2-(Δ^3-Cyclohexenyl)ethyl Isothiocyanate (10). A 4.80-g (0.038 mol) portion of crude amine, prepared by reduction of 1.5 g of 2-(Δ^3-cyclohexenyl)acetonitrile, was treated with carbon disulfide, potassium hydroxide, and ethyl chloroformate according to a known procedure.[7] Distillation of the crude material gave 1.935 g (30%) of product: bp 92–93° (1.4 mm); infrared spectrum (film) 3020, 2910, 2090, 1345, and 1095 cm^{-1}; nmr (CCl_4) τ 4.35 (s), 6.40 (tr), 7.53–9.03 (mult).

Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.81; N, 8.38; S, 19.18. Found: C, 64.85; H, 8.06; N, 8.19; S, 18.90.

1-[2-(Δ^3-Cyclohexenyl)ethyl]-3-(1-adamantyl)thiourea. A solution of 0.604 g (0.004 mol) of 1-adamantylamine and 0.334 g (0.002 mol) of **10** in 20 ml of dry dioxane was stirred at room temperature overnight. The mixture was added to water and extracted with ether. The ether solution was dried and concentrated giving a light-brown solid. Recrystallization from ether–pentane afforded the thiourea as white crystals, mp 94–95°.

Anal. Calcd for $C_{19}H_{30}N_2S$: C, 71.64; H, 9.49; N, 8.80; S, 10.07. Found: C, 71.76; H, 9.29; N, 8.86; S, 10.06.

Bicyclo[2.2.2]oct-2-yl Thiocyanate (11). To 7.81 g (0.127 mol) of cyanogen chloride dissolved in 50 ml of anhydrous ether and being stirred at 0° was added dropwise a mixture of 7.04 g (0.070 mol) of triethylamine and 9.0 g (0.063 mol) of bicyclo[2.2.2]octane-2-thiol.[16] After addition was complete, the mixture was allowed to come to room temperature where it was stirred for 3 hr. The resultant slurry was then washed with water, saturated sodium bicarbonate solution, and then dried over magnesium sulfate. Evaporation of the solvent gave 11.4 g of crude material which was distilled at 82–83° (0.8 mm), affording 6.02 g (57%) of **11** as a colorless liquid: infrared spectrum (film) 2895, 2140, 1265, and 960 cm^{-1}; nmr (CCl_4) τ 6.28 (dd), 7.35–8.88 (mult).

Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.81; N, 8.38; S, 19.18. Found: C, 64.78; H, 8.01; N, 8.88; S, 19.04.

Bicyclo[2.2.2]oct-2-yl Isothiocyanate (12). A 0.750-g (0.006 mol) sample of bicyclo[2.2.2]oct-2-ylamine, prepared by the catalytic hydrogenation of ethyl N-bicyclo[2.2.2]oct-2-en-5-ylcarbamate[17] followed by basic hydrolysis, was subjected to a previously described procedure[7] affording 0.432 g (43%) of **12** as a white solid: mp 74–75°; infrared spectrum (CCl_4) 2870, 2080, and 1310 cm^{-1}; nmr (CCl_4) τ 6.16 (br mult), 7.57–8.83 (mult).

Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.81; N, 8.38; S, 19.18. Found: C, 64.91; H, 7.81; N, 8.38; S, 19.05.

1-(Bicyclo[2.2.2]oct-2-yl)-3-*t*-butylthiourea. A mixture of 0.239 g (0.0014 mol) of **12**, 0.157 g (0.0022 mol) of *t*-butylamine, and 15 ml of dry dioxane was allowed to react according to the adamantylthiourea procedure described above. Recrystallization from ether–pentane gave the desired product as white needles, mp 161.5–162°.

Anal. Calcd for $C_{13}H_{24}N_2S$: C, 64.95; H, 10.06; N, 11.65; S, 13.34. Found: C, 65.03; H, 9.88; N, 11.67; S, 13.04.

***exo*-Bicyclo[3.2.1]oct-3-en-2-yl Thiolacetate.** A mixture of 23.25 g (0.215 mol) of bicyclo[3.2.1]oct-2-ene,[18] 26.79 g (0.150 mol) of N-bromosuccinimide, 0.254 g of benzoyl peroxide, and 130 ml of carbon tetrachloride was heated at reflux. After approximately 30 min a spontaneous reaction occurred and the heating was stopped. The reaction mixture was stirred for an additional 45 min and then rapidly filtered to remove the succinimide. The unstable crude bromide solution was added to a solution of 196.0 g (2.0 mol) of sodium thiolacetate in 225 ml of water, and stirred vigorously at room temperature overnight. After addition to 150 ml of water, the carbon tetrachloride layer was separated, and the aqueous layer extracted with pentane. The combined pentane and carbon tetrachloride extracts were washed with saturated sodium bicarbonate and then dried and concentrated. The residue was distilled at 68–70° (0.5 mm), giving 16.18 g (59%) of an orange liquid which was shown by gc analysis to contain approximately 4% of the corresponding unsaturated alcohol.

***exo*-Bicyclo[3.2.1]octane-2-thiol (15).** The reaction of 5.460 g (0.03 mol) of the distilled thiolacetate with potassium azodicarboxylate[19] gave 4.93 g of crude material as a yellow liquid. Infrared analysis indicated the complete reduction of the thiol ester and approximately 65% reduction of the double bond.[20]

***exo*-Bicyclo[3.2.1]oct-2-yl Thiocyanate (13).** A 4.93-g (0.035 mol) portion of the previous thiol mixture was treated with 3.91 g (0.039 mol) of triethylamine and 4.33 g (0.070 mol) of cyanogen chloride by the usual method. The crude product (6.53 g) was purified by chromatography on silica gel and the saturated thiocyanate distilled at 68–70° (0.1 mm) giving 1.54 g of a colorless liquid: infrared spectrum (film) 2910, 2150, and 755 cm^{-1}; nmr (CCl_4) τ 6.30 (n mult), 7.07–8.91 (br mult).

Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.81; N, 8.38; S, 19.18. Found: C, 64.74; H, 7.90, N, 8.45; S, 18.91.

***exo*-Bicyclo[3.2.1]oct-2-yl Isothiocyanate (14).** A carbon tetrachloride solution of the bromide, prepared from 19.30 g (0.179 mol) of bicyclo[3.2.1]oct-2-ene in the manner mentioned above, was added to 41.22 g (0.63 mol) of sodium azide in 120 ml of water and the resulting mixture vigorously stirred at room temperature overnight. The carbon tetrachloride layer was separated and the aqueous layer extracted with pentane. The combined carbon tetrachloride and pentane extracts were dried, concentrated, and the residue was distilled at 55–58° (1.0 mm) giving 9.640 g (52%) of *exo*-bicyclo[3.2.1]-3-en-2-yl azide as a yellow liquid.

A solution of 9.640 g (0.065 mol) of the azide in 120 ml of anhydrous ether was added dropwise to a suspension of 4.917 g (0.129 mol) of lithium aluminum hydride in 250 ml of anhydrous ether and the reaction mixture stirred at reflux for 45 hr. After cooling, 5 ml of water was carefully added, followed by 15 ml of 15% potassium hydroxide solution and then another 5 ml of water. The resultant white precipitate was removed by filtration and thoroughly washed with ether. To the combined ether solution was added 7.930 g (0.065 mol) of benzoic acid. Upon standing at room temperature, a white solid formed slowly and was collected by filtration giving 7.561 g of the benzoate salt of the unsaturated amine as white flakes, mp 153.5–155° dec. Evaporation of the filtrate gave 2.4 g of unreacted azide which was subsequently recycled.

A mixture of 7.427 g (0.030 mol) of the above benzoate salt, 0.743 g of platinum oxide, and 200 ml of methanol was hydrogenated at 40 psi for 20 hr. The catalyst was removed by filtration and the methanol concentrated. The crude product was recrystallized from chloroform–ether, giving 6.778 g (91%) of the saturated benzoate salt as a white powder, mp 193–194° dec. This salt was treated with sufficient potassium hydroxide to liberate the free amine, which was recovered by extraction with ether and dried. The ether was concentrated by distillation. The crude product was sublimed at 70° (760 mm), affording 1.645 g (52%) of *exo*-bicyclo[3.2.1]oct-2-ylamine as a waxy, white solid.

A 1.645-g (0.0132 mol) sample of amine was treated with 2.710 g (0.0132 mol) of N,N′-dicyclohexylcarbodiimide and 10.00 g (0.0132 mol) of carbon disulfide according to a previously published procedure.[7] The crude product was partially purified by chromatography on silica gel, giving 1.770 g (80%) of a colorless liquid, bp 79–83° (0.8 mm). An analytical sample was obtained by collection on gc, giving a white solid: mp 51.5–52°; bp 66–67° (0.2 mm); infrared spectrum (CCl_4) 2900, 2080, 1325, and 935 cm^{-1}; nmr (CCl_4) τ 6.33 (n mult), 7.17–8.92 (br mult).

Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.81; N, 8.38; S, 19.18. Found: C, 64.88; H, 7.90; N, 8.74; S, 19.41.

1-(*exo*-Bicyclo[3.2.1]oct-2-yl)-3-*t*-butylthiourea. A mixture of 83 mg (0.5 mmol) of **14**, 54.8 mg (0.75 mmol) of *t*-butylamine, and

(16) Prepared by thiolacetic acid addition to bicyclo[2.2.2]octene followed by reduction with lithium aluminum hydride.

(17) H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Amer. Chem. Soc.*, **83**, 1391 (1961).

(18) C. W. Jefford, D. T. Hill, and J. Gunsher, *ibid.*, **89**, 6881 (1967).

(19) J. Thiele, *Justus Liebigs Ann. Chem.*, **271**, 127 (1892).

(20) To our knowledge, this is the first time that ester cleavage has been observed in preference to carbon–carbon double bond reduction with any diimide source.

5 ml of dry dioxane was allowed to react by the method previously described. Recrystallization from ether–pentane gave 110 mg (92%) of the desired material as white needles, mp 163–163.5°.

Anal. Calcd for $C_{13}H_{24}N_2S$: C, 64.95; H, 10.06; N, 11.65. Found: C, 64.99; H, 10.04; N, 11.77.

***endo*-Bicyclo[3.2.1]oct-2-yl Thiocyanate (18).** A mixture of 4.20 g (0.015 mol) of Δ^4-cycloheptenylcarbinyl *p*-toluenesulfonate,[21] 1.746 g (0.018 mol) of potassium thiocyanate, and 25 ml of sulfolane was allowed to react as in the preparation of **9**, affording 2.53 g of crude Δ^4-cycloheptenylcarbinyl thiocyanate (**17**). A 1.00-g portion of the crude thiocyanate dissolved in 40 ml of sulfolane was sealed in a glass tube and heated at 150° for 32 hr. The contents of the tube were added to water and extracted with pentane. Concentration of the combined extracts, followed by distillation at 62–70° (0.15 mm), gave 400 mg of a mixture consisting of 9% **19**, 52% Δ^4-cycloheptenylcarbinyl isothiocyanate, 37% **18**, and 2% unreacted starting material. The thiocyanates were separated from the isothiocyanates by chromatography on silica gel, and the combined thiocyanate fractions were treated with a solution of bromine in carbon tetrachloride. This procedure gave 290 mg of a yellow liquid upon removal of the solvent. Distillation of this crude material at 67–70° (0.15 mm) afforded 90 mg of pure **18**: infrared spectrum (film) 2910, 2140, 1045, and 765 cm^{-1}; nmr (CCl_4) τ 6.42 (br mult), 7.33–8.93 (br mult).

Anal. Calcd for $C_9H_{13}NS$: C, 64.92; H, 7.81; N, 8.38. Found: C, 64.71; H, 7.95; N, 8.62.

***endo*-Bicyclo[3.2.1]oct-2-yl Isothiocyanate (19).** A 2.93-g (0.023 mol) portion of *endo*-bicyclo[3.2.1]oct-2-ylamine[22] was treated with carbon disulfide and ethyl chloroformate by a previously described procedure,[7] giving 2.38 g (60%) of a semisolid product. Recrystallization from pentane afforded a white solid: mp 70–71°; infrared spectrum (CCl_4) 2910, 2060, and 1325 cm^{-1}; nmr (CCl_4) τ 6.28 (br tr), 7.35–9.0 (mult).

Anal. Calcd for $C_9H_{13}NS$: C, 64.62; H, 7.81; N, 8.38. Found: C, 64.74; H, 7.71; N, 8.27.

(21) L. A. Spurlock, Ph.D. Thesis, Wayne State University, Detroit, Mich., 1963.

(22) F. Derichs and H. Bueren, *Chem. Abstr.*, **61**, 593*e* (1964).

1-(*endo*-Bicyclo[3.2.1]oct-2-yl)-3-*t*-butylthiourea. The derivative was prepared by the method previously described, giving a white solid, mp 162.5–163.0°.

Anal. Calcd for $C_{13}H_{24}N_2S$: C, 64.95; H, 10.06; N, 11.65. Found: C, 64.93; H, 9.99; N, 11.60.

Isomerization of 9, 11, and 13. Solutions 0.15 *M* in pure **9**, **11**, or **13** were prepared using the various solvents. Aliquots (1 ml) were sealed in glass tubes and heated at constant temperatures for different lengths of time. The contents of the tubes were poured into 25 ml of water and the products were extracted with two 5-ml portions of pentane. The combined extracts were washed with water, dried, and concentrated. Residues were examined by gc using the following conditions: column 50 ft × 0.02 in. butanediol succinate; temperature 160°; carrier flow 65 lb He; R_t (min) **14** 6.2, **12** and **19** 6.5, **10** 7.9, **11** 9.8, **18** 10.2, **13** 10.6, **9** 11.6.

Catalyzed Isomerizations of 9, 11, and 13 in Benzene. A 0.15 *M* solution of the pure thiocyanate in benzene, which was 2% in boron trifluoride, was heated at reflux. Samples (1 ml) were withdrawn at various intervals. The samples were mixed with 10 ml of pentane, washed with saturated sodium bicarbonate solution, and dried. Upon concentration, analyses were conducted by gc using the above conditions.

Kinetic Procedure. Aliquots (5 ml) of sulfolane solutions 0.04 *M* in **11**, or 4-ml aliquots of sulfolane solutions 0.036 *M* in **13**, were sealed in glass tubes and heated at 130.0 and 150.0°. Tubes were removed at intervals and quenched by immersion in ice. The tubes were opened and the contents added to 100 ml of water. Products were extracted with pentane and the combined extracts washed with water, dried, and concentrated. The residues were examined by gc using the following conditions: column 6 ft × 0.25 in. 10% XE-60 on Diatoport S; temperature 200°; carrier flow 110 ml/min; R_t (min) **12** and **14** 5.6, **11** and **13** 8.2.

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Aromatic Protonation. VI. Brønsted Relation for Aromatic Hydrogen Exchange in 1,3,5-Trimethoxybenzene[1]

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Abstract: The Brønsted relation for acid-catalyzed detritiation of 1,3,5-trimethoxybenzene-2-*t* has been reinvestigated by determining rate constants for catalysis by eight new acids and revising the value for a previously used catalyst. This change and the addition of these new catalytic coefficients do not significantly alter the exponent in the overall Brønsted relation for this reaction (original value: 0.52 ± 0.01;[4b] new value: 0.56 ± 0.03), but they do reveal striking deviations characteristic of catalyst type. Correlations based on subsets of data give Brønsted exponents ranging from 0.56 to 0.71. This suggests that the extent of proton transfer at the transition state of a proton-transfer reaction may be a function of catalyst type, and that overall Brønsted exponents can therefore provide only an approximate measure of this transition state property.

Several years ago we discovered that aromatic hydrogen exchange is subject to general acid catalysis.[4] Our interest in this reaction at that time was chiefly in its mechanism, but in the course of our work we measured several catalytic coefficients for the detritiation of 1,3,5-trimethoxybenzene-2-*t* and published a Brønsted plot.[4b] This Brønsted plot was the first ever constructed for an authentic rate-limiting proton transfer from acid to substrate (A-SE2 mechanism) and it was unusual in that it was accurately linear over the

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