Experimental Section

Nmr single resonance spectra were obtained on Varian HA 100 (^{1}H) and A56-50 (^{19}F) spectrometers. ^{1}H(^{19}F), ^{19}F(^{1}H), and ^{19}F(^{19}F) double-resonance experiments were performed on a Varian HA-60 instrument operating at 56.4 and 60.0 MHz. Octafluorocyclobutane, CCl_3F, CF_2ClCF_2Cl, and $C_6H_5CF_3$ were used as lock signals for the ^{19}F experiments. The necessary irradiating field for the heteronuclear decoupling experiments was provided by a NMR Specialties Model SD-60B heteronuclear spin decoupler. All of the benzotrifluorides **5** were obtained from Columbia Organic Chemicals.

α,α-Difluorotoluene was prepared from benzaldehyde and SF_4.[15]

α,α,α-Difluorochlorotoluene. In a three-necked, 250-ml flask equipped with a thermometer, gas inlet tube, and reflux condensor was placed 30 ml of α,α-difluorotoluene and 50 mg of azobisisobutyronitrile. The flask was then heated to 70° while chlorine gas was bubbled through the reaction mixture. The reaction was followed by ^{19}F nmr and by testing the effluent gas for HCl and was found to be over in about 90 min. The product was then distilled: bp 140°, 61° (50 mm); nmr (CCl_3) multiplet δ 7.5, ^{19}F φ 49.36.

2,3,4,5,6-Pentafluorobenzyl Fluoride. The apparatus consisted of a 250-ml, three-necked flask equipped with an addition funnel, a motor-driven stirrer, and an exit tube leading to a Dry Ice trap connected to a vacuum pump. The apparatus was flushed with dry nitrogen and then 48 g (0.2 mol) of finely powdered HgF_2 was placed in the flask and 10 g (0.04 mol) pentafluorobenzyl bromide (Penninsular Chem Research) was placed in the funnel. After evacuation of the flask the bromide was then added dropwise to the rapidly stirred mercuric fluoride over a period of 15 min. The product which collected in the Dry Ice trap was then filtered from a few grams of NaF, yield 1.8 g (45%). The nmr spectrum is given in Table IV.

Decafluorobenzhydrol was obtained from Imperial Smelters Ltd.

Tris(pentafluorophenyl)carbinol was a gift from Professor R. Filler.[12]

α,α-Difluoroethylbenzene was prepared from HF and phenylacetylene according to Matsuda, *et al.*[16] A procedural change suggested in ref 27 of this paper was followed and resulted in a yield of 24% rather than the 18% reported.

α,α-Dichloroethylbenzene. A solution of 50 g of phenylacetylene in 100 ml of methylene chloride was cooled to −40° and saturated with anhydrous HCl for 4 hr. After removal of the solvent and excess HCl on a rotary evaporator, the product was vacuum distilled. After collection of a small portion of α-chlorostyrene the product was collected and then redistilled: bp 71° (4 mm), 50° (1 mm); nmr (CCl_4) multiplet 7.68 (2), multiplet 7.28 (3), 2.50 (3), yield 75%. The **α-chlorostyrene** fraction was redistilled: bp 98° (46 mm); nmr (CCl_4) multiplet 7.55 (2), multiplet 7.25 (3), doublet 5.67 (1), doublet 5.44 (1), yield 10%. The title compound should be stored at 0°.

α,α-Dibromoethylbenzene was prepared from anhydrous HBr and phenylacetylene using a procedure analogous to the one used for preparing α,α-dichloroethylbenzene, yields: α,α-dibromoethylbenzene, bp 76° (0.15 mm); nmr (CCl_4) multiplet 7.70 (2), multiplet 7.25 (3), 3.94 (3), 25%; **α-bromostyrene**, bp 61° (0.5 mm); nmr (CCl_4) multiplet 7.52 (2), multiplet 7.25 (3), doublet 6.03 (1), doublet 5.71 (1), 60%. The title compound should be stored at 0°.

2,2-Dihalopropanes. The fluorine compound was prepared according to the literature[15] from acetone and SF_4. The chlorine compound was obtained from J. T. Baker and the bromine compound from K and K Laboratories.

Dihalodiphenylmethanes. The fluorine compound was prepared from SF_4 and benzophenone.[15] The chlorine compound was obtained from Frinton Laboratories and distilled before use.

Acknowledgment. Support of this research by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society is greatly appreciated. Professor R. Filler is thanked for the sample of tris(pentafluorophenyl)carbinol.

(15) W. R. Hasek, W. C. Smith, and V. A. Englehardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960).

(16) K. Matsuda, J. A. Dedlak, J. S. Noland, and E. C. Glocker, *J. Org. Chem.*, 27, 4018 (1962).

The Nature of the Carbonium Ion. I. The π-Route Norbornyl Cation from a Thiocyanate–Isothiocyanate Isomerization

Langley A. Spurlock and Walter G. Cox

Contribution from the Department of Chemistry, Temple University of the Commonwealth System of Higher Education, Philadelphia, Pennsylvania 19122. *Received October 10, 1968*

Abstract: 2-(Δ^3-Cyclopentenyl)ethyl thiocyanate was isomerized to a mixture of *exo*-2-norbornyl thiocyanate, *exo*-2-norbornyl isothiocyanate, and 2-(Δ^3-cyclopentenyl)ethyl isothiocyanate in a variety of solvents. No *endo*-norbornyl products were detected. The rate of reaction and product composition were directly governed by the solvent employed. The necessity of the double bond for isomerization was established by the failure of the saturated 2-cyclopentylethyl thiocyanate to isomerize under these conditions. Rate measurements confirmed the isomerization as a first-order process and activation parameters were calculated. The catalytic effects of potassium perchlorate, potassium thiocyanate, and boron trifluoride were studied and the results were used in deducing the nature of the norbornyl cations which serve as intermediates for isomerization.

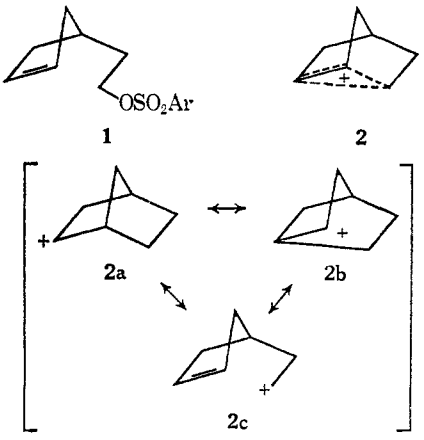
Prior investigations have given evidence that the thermal rearrangements of alkyl thiocyanates to their isomeric isothiocyanates can proceed by several mechanistic pathways. It can be seen that the choice of isomerization mode is dependent on the structure of the alkyl moiety, the nature of the solvent employed as an isomerizing medium, and on catalysts. In the cases of most allylic thiocyanates, rearrangement occurs by way of a six-membered cyclic transition state involving little to no charge separation.[1,2] These reactions are therefore relatively insensitive to solvent and catalyst effects.[3,4a] Nonallylic thiocyanates present a

(1) O. Billeter, *Helv. Chim. Acta*, **8**, 337 (1925).
(2) O. Mumm and H. Richter, *Ber.*, 73, 843 (1940).
(3) P. A. S. Smith and D. W. Emerson, *J. Am. Chem. Soc.*, **82**, 3076 (1960).

somewhat more complicated picture. Their conversion to isothiocyanates is strongly solvent influenced, and is often catalyzed by the Lewis base thiocyanate ion[4] as well as by Lewis acids.[5] The over-all aspect of these isomerizations is one of a kinetically favored thiocyanate with a relatively weak carbon–sulfur bond proceeding *via* bimolecular displacement or unimolecular dissociation–recombination to the thermodynamically favored isothiocyanate.

Intensive investigation of the benzhydryl thiocyanates by Fava, Iliceto, and coworkers[4] has revealed that they undergo ionization with formation of ion pairs followed by recombination to give the corresponding isothiocyanates. It was estimated that only a small fraction of the ion pairs in this system, which can produce a relatively stable intermediate carbonium ion, proceed to degrees of dissociation past the intimate pair stage. Our own observation that cyclopropylcarbinyl thiocyanate, in contrast to most derivatives of this skeleton, gives primarily unrearranged product[6] would seem to bear out the notion of closely associated ionic intermediates.

To further explore this possibility we wished to examine thiocyanate isomerizations in which participation by a remote double bond supplies a nucleophilic driving force for the ionization. Principal analogies for this process may be found in reports[7] that the solvolyses of 2-(Δ^3-cyclopentenyl)ethyl arylsulfonates (**1**) proceed at rates substantially faster than their saturated analogs giving nearly exclusively cyclized product. Explanations for these observations,

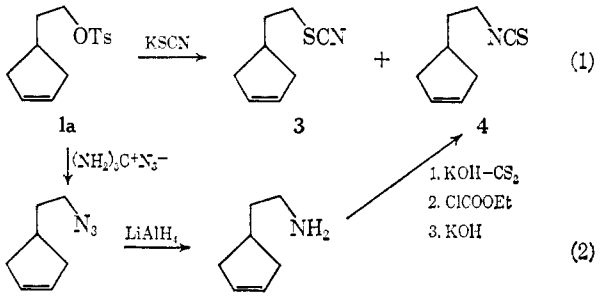


subsequently elaborated,[8] have assumed a large degree of π-electron participation in the transition states, and mainly the intermediacy of species resembling the bridged ion **2**. This bridged representation can also be described in valence bond notation (**2a–c**) with each limiting structure corresponding to a starting material from which the ion may be generated and, in theory, corresponding to a possible product derived from this ion. That the product derived from **2c** is virtually never obtained from solvolyses of any of the starting materials casts doubt on the representation of the fully formed ion as having this limiting structure. Correspondingly, many authors have adopted the bridged notation eliminating this form. The desirability of thiocyanate ionizations for possible clarification of this point is indicated by the predominant intimate-pair status of intermediates, rendering the thiocyanate ion an effective carbonium ion "trap." The choice of 2-(Δ^3-cyclopentenyl)ethyl thiocyanate (**3**) was thus dictated by the wealth of information already available for ionic dissociations involving this carbon skeleton and the ease of synthesis from the known esters **1**.

Results

The *p*-toluenesulfonate **1a**, precursor of 2-(Δ^3-cyclopentenyl)ethyl thiocyanate (**3**), was prepared from 2-(Δ^3-cyclopentenyl)ethanol.[7] Treatment of **1a** with potassium thiocyanate in acetone or sulfolane gave a 96:4 ratio of **3** to isothiocyanate **4** (Scheme I, eq 1). Separation of this mixture by chromatography on silica gel or by preferential reaction of **4** with alkyl amines gave pure **3**. 2-(Δ^3-Cyclopentenyl)ethyl isothiocyanate (**4**) was also prepared by the reaction of carbon disulfide, ethyl chloroformate, and potassium hydroxide with the corresponding amine (eq 2). The isothiocyanate **4**,

Scheme I



obtained in this manner, was identical with the minor product of the potassium thiocyanate reaction with **1a**.

Authentic samples of the four plausible cyclized products were obtained by the methods shown in Scheme II. *exo*-2-Norbornyl thiocyanate (**5**) and isothiocyanate (**6**) were prepared by potassium thiocyanate displacement on *endo*-2-norbornyl *p*-bromobenzenesulfonate[9] in acetone (eq 3). The preparation of isomerically pure *endo*-2-norbornyl thiocyanate (**7**) (eq 4) proceeded from the cycloaddition of cyclopentadiene with vinyl thiolacetate[10] giving mainly *endo*-2-norbornen-5-yl thiolacetate. This was followed by simultaneous diimide reduction of the double bond and thiolester to the 2-norbornyl thiols, and then cyanogen chloride treatment. The resulting mixture of 2-norbornyl thiocyanates (*endo*/*exo* = ~2) was heated to preferentially isomerize the *exo* compound, and pure **7** was obtained by reaction of the isomerization product **6** with *n*-butylamine followed by separation of the crystalline *exo*-2-norbornyl-*n*-butyl-

(4) (a) A. Iliceto, A. Fava, and U. Mazzucato, *Tetrahedron Letters*, 27 (1960); (b) A. Iliceto, A. Fava, U. Mazzucato, and P. Radici, *Gazz. Chim. Ital.*, **99**, 919 (1960); (c) A. Iliceto, A. Fava, U. Mazzucato, and O. Rosseto, *J. Am. Chem. Soc.*, **83**, 2729 (1961); (d) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *ibid.*, **87**, 1045 (1965); (e) A. Fava, A. Iliceto, and S. Bresadola, *ibid.*, **87**, 4791 (1965).

(5) A. Smits and H. Vixseboxe, *Verslag Koninkl. Akad. Wetenschap.*, 46 (1913); *Chem. Abstr.*, **8**, 649 (1914); J. Gillis, *Rec. Trav. Chim.*, **39**, 330 (1920); E. Schmidt, W. Striewsky, M. Secfelder, and F. Hitzler, *Ann.*, **568**, 192 (1950).

(6) L. A. Spurlock and P. E. Newallis, *Tetrahedron Letters*, 303 (1966).

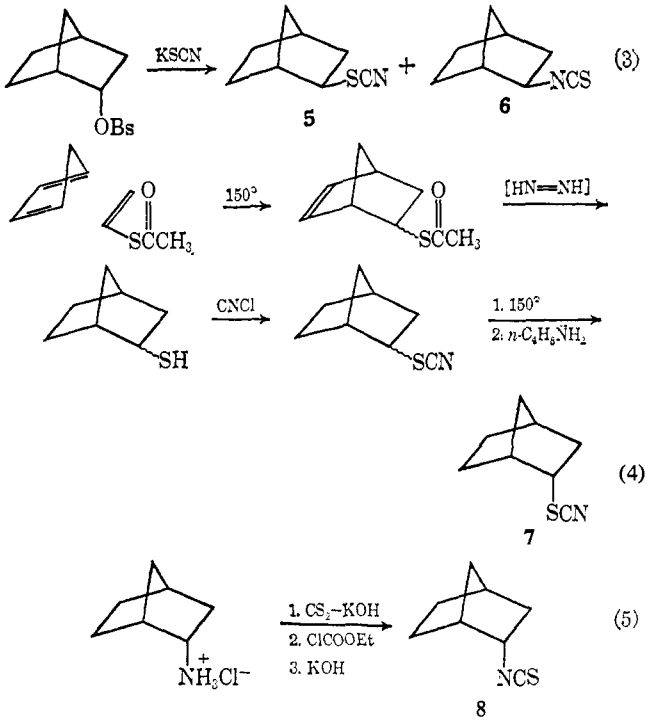
(7) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

(8) (a) P. D. Bartlett, S. Bank, R. J. Crawford, and G. H. Schmid, *ibid.*, **87**, 1288 (1965); (b) K. Humski, S. Borcic, and D. Sunko, *Croat. Chem. Acta*, **37**, 3 (1965); (c) C. C. Lee and L. K. M. Lam, *J. Am. Chem. Soc.*, **88**, 2834 (1966).

(9) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, 74, 1127 (1952).

(10) H. Bohme, J. Roehr, and W. Schlephacle, *Ann.*, **648**, 15 (1961).

Scheme II



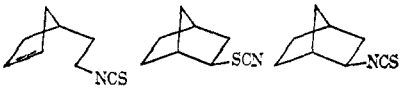
thiourea. Pure *endo*-2-norbornyl isothiocyanate (**8**) was prepared from commerical *endo*-2-norbornylamine hydrochloride by the method previously described (eq 5). The saturated compounds, 2-cyclopentylethyl thiocyanate (**9**) and isothiocyanate (**10**), were prepared from 2-cyclopentylethanol[3a] by methods analo-

9 **10**

gous to those used for **3** and **4**, respectively. Infrared and nmr spectra (see Experimental Section) for all compounds were in accord with the structural assignments and minimum purity in excess of 99.5% could be confirmed by gc and elemental analyses.

Table I summarizes the results of solvent influence studies on the relative product ratios and isomerization rates of thiocyanate **3**. In these control experiments, solutions 0.15 *M* in **3** were sealed in ampoules and heated at 150.4°. The isomerization mixtures were then analyzed by gc and the identities of products were confirmed by comparison of their retention times with those of authentic materials on two different columns. Values listed are the averages of at least three runs with over-all material recovery 96–99%. The uncyclized product ratios could be shown as characteristic only of the solvent. The ratio of **4** to the combined cyclized products **5** and **6** was unchanged over the range of isomerization (5–80%) examined in additional control experiments in sulfolane and dimethylformamide. Variation of the concentration of **3** (0.15–0.015 *M*) likewise gave no change in product ratios from those shown in Table I. The relative ratio of *cyclized* products was found to be time dependent, however, favoring isothiocyanate **6** over thiocyanate **5** with increasing reaction time. Independent studies[11] with *exo*-norbornyl thiocyanate (**5**) have revealed that under these conditions it gives only its isomeric isothiocyanate **6** at a rate approximately five times the isomerization rate of **3**. The change of the **6**/**5** ratio is therefore easily explained as resulting from a secondary process. The more accurate estimates of initial product distribution are probably obtained from runs proceeding to <10% reaction, as is witnessed by the behavior of first-order rate plots discussed later.

Table I. Isomerizations of 0.15 *M* Solutions of **3** at 150.4°



Solvent	Time, hr	Rel product ratio			% isomerization
Tetramethylurea	24	40.0	56.6	3.4	6.0
Acetonitrile	24	5.5	43.5	51.0	7.2
Dimethylacetamide	24	61.7	24.1	14.2	14.7
Dimethylformamide	24	59.0	24.2	16.8	16.6
	12	58.1	30.2	12.7	5.1
Sulfolane	24	3.8	21.0	75.2	37.7
	5	3.8	31.4	64.6	5.0

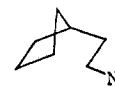
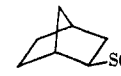
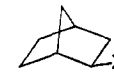
In none of the solvents employed could either of the *endo*-2-norbornyl derivatives **7** or **8** be found within the limits of gc detection (0.5%). Both compounds were completely stable to the reaction conditions and the thiocyanate **7** could not be made to undergo isomerization under any conditions. The saturated thiocyanate **9** was similarly inert to conditions conducive to the isomerization of **3**. More drastic attempts to effect isomerization of **9** at temperatures in excess of 165° resulted in extensive decomposition but no detectable isomerization.

The effects of catalysts on the isomerizations of the unsaturated thiocyanate **3** and its saturated analog **9** were explored. Conditions were similar to those outlined for the uncatalyzed isomerizations, but with various substances dissolved in the solvent. Results are tabulated in Table II. Those solutions of **3** to which potassium thiocyanate was added showed a time-dependent ratio of uncyclized product **4** to the cyclized compounds **5** and **6** in addition to the previously observed time dependent **6**/**5** ratio. That this additional variable was due to competing displacement (giving **4**) and dissociation (giving predominantly **5** and **6**) processes could be confirmed by subjecting the saturated compound, **9**, to identical conditions. The rapid formation in this medium of isothiocyanate **10**, from **9** indicated that for primary thiocyanates the principal mode of thiocyanate ion catalysis is by the displacement pathway. The further observation that the presence of potassium perchlorate in the isomerizing solution has no appreciable effect on the rate or products from **3** would seem to rule out any additional special salt effects.

Solutions of **3** in benzene, 0.3*M* in boron trifluoride, were heated at reflux and observed slowly to undergo isomerization. The influence of the Lewis acid is quite striking since in benzene alone, the thiocyanate would not isomerize to any detectable extent even at 150°. The only products of isomerization under these conditions are the cyclized thiocyanate **5** and isothi-

(11) L. A. Spurlock and T. E. Parks, to be published.

Table II. Catalyzed Isomerizations of 0.15 *M* Solutions of **3** and **9**

Solvent	Catalyst (concn, *M*)	Time, hr	Temp, °C	Rel product ratio 			% isomerization
3							
Sulfolane	KSCN (0.1)	19	150.0	50.9	11.9	37.2	58.5
		24		55.3	9.1	35.5	70.2
	$KClO_4$ (0.1)	24	150.0	4.2	21.0	74.8	38.3
Benzene	BF_3 (0.3)	14	80.1		43.7	56.3	7.0
		24			40.7	59.3	10.3
		45			23.5	76.5	28.5
		95			16.2	83.8	47.3
9							
Sulfolane	KSCN (0.1)	24	150.0				47.0[a]

[a] The sole product was isothiocyanate **10**.

ocyanate **6**. Their time dependent ratio could again be shown to be the result of the subsequent isomerization of initially formed **5**.

Table III summarizes the results from rate studies of the isomerization of **3**. Rate measurements in solvents other than sulfolane proved to be unsatisfactory due

Table III. Rate Studies of the Isomerization of **3** in Sulfolane

Temp, °C	Catalyst	$k \times 10^6$ sec^{-1}	$t_{1/2}$, hr
150.5		5.02 ± 0.11	38
130.3		0.87 ± 0.01	221
149.8	$KClO_4$ (0.01 *M*)	7.29 ± 0.11	27
ΔH^* = 29.5 kcal/mole		ΔS^* = −13.9 eu	

either to the sluggishness of the reaction (acetonitrile, tetramethylurea) or to accompanying side reactions (dimethylformamide, dimethylacetamide, dimethyl sulfoxide). The reaction was followed by titration, with visual indicator, of standard *n*-butylamine which was consumed by the product isothiocyanates when added to the isomerized mixture.[12]

Graphs (log [RSCN] *vs. t*) of the data showed linear first-order behavior for the first 5–7% reaction followed by a gradual downward drift attributable to the formation of the more rapidly isomerizing norbornyl thiocyanate (**5**). Accordingly, values given in Table III are calculated from the early portion of the reaction.

Discussion

The strong influence of solvent polarity on the rate of reaction and on product distribution leaves little doubt that this isomerization proceeds *via* ionic intermediates generated from the neutral thiocyanate molecule. The lack of concentration dependence over a large (100-fold) range of dilute solutions supports this concept admirably. The major concern, therefore, lies only with the nature of the cationic intermediates. That few if any of these intermediates dissociate past the intimate pair stage seems probable by analogy to the previously mentioned benzhydryl thiocyanate studies.[4c]

Clearly, the π-route norbornyl cation is implicated by the formation of norbornyl products, and the necessity for the remote double bond as a nucleophilic driving force to ionization. The utter failure to obtain isomerization with the saturated analog **9** also removes the possibility of an initial "unassisted" (assisted only by solvent) ionization playing any part in the reaction. The formation of uncyclized isothiocyanate **4** is unusual considering the completely cyclized products from solvolyses of the corresponding arylsulfonates.[7] This fact becomes, therefore, more interesting when one realizes that its formation is dependent upon double-bond participation just as are the cyclized products **5** and **6**. The failure of *exo*-norbornyl thiocyanate (**5**) to produce any detectable amounts of **4** would seem to indicate that only the "π-route" norbornyl ion supports attack by the nucleophile at C_6. Rationale for this may be found in the relative positions of the leaving group nucleophile in the initially formed tight ion pairs. When the ion pair is formed directly from **3**, the initial position of the anion is immediate to the original primary carbon (C_6). This thiocyanate ion is in a favorable position to reattach itself and, because of its "solvation" of the electronic charge at C_6, may render the carbon more electrophilic than in the usual π-route norbornyl cations.[13] A representation of this sort of ion (**11a**) is shown in Scheme III. The cyclized products must be derived from an ion pair in which the thiocyanate ion is located at the C_2–C_3 *exo* face of the norbornyl skeleton (**11b**). As this probably corresponds to the same pair initially derived from ionization of **5** it seems reasonable to include it as a single representation derived reversibly from **5**, but irreversibly from **11a** (hence, **3**).[14a] An alternate representation for **11a** as a π-complex carbonium ion (**11c**)[14b] remains a possibility but seems an unnecessary complication of the existing scheme.

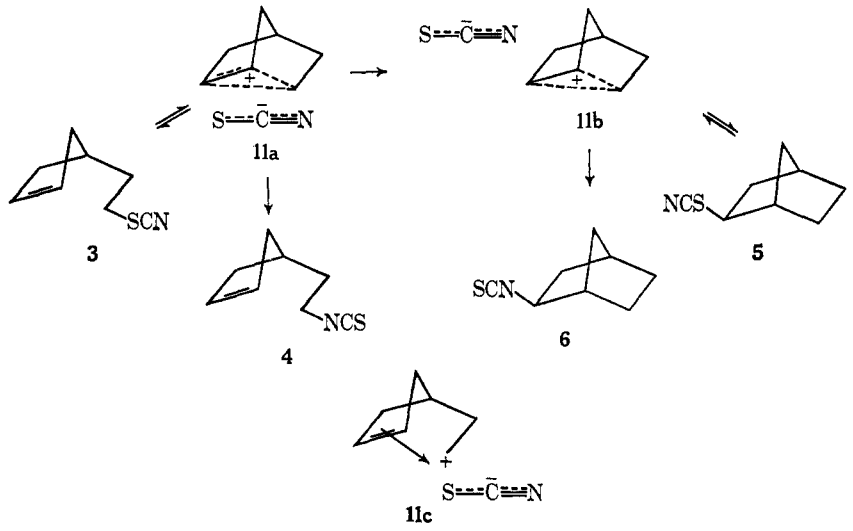
The catalytic effects of the nonnucleophilic potassium perchlorate and the electrophilic boron trifluoride again

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

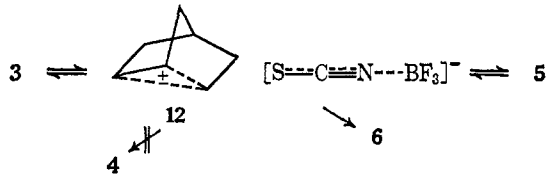
(13) It has been estimated by Bartlett, *et al.*,[8a] that C_6 is only one-third as "carbonium-ion-like" as the original double-bond carbons in the transition state for assisted ionization of the arylsulfonates.

(14) A referee has suggested an alternative to this explanation involving a 6,2 hydride shift as the occurence responsible for formation of **5** and **6**. The two norbornyl cations in this case would be represented as **11a**, giving **4**, and an edge-protonated nortricyclene, giving cyclized products. Doubt is cast upon this possibility by our recent[11] deuterium-labeling experiments indicating that no hydride shifts occur during isomerizations of **5**. It seems therefore unlikely that similar shifts could play a dominant role in the interconversions of ions derived from **3**. Nevertheless the results of labeling experiments on **3** will be reported along with the details of the results from **5** in a subsequent paper of this series. (b) This representation was presented by Bartlett, *et al.*,[8n] but rejected, in their instance, since it could not be experimentally detected.

Scheme III

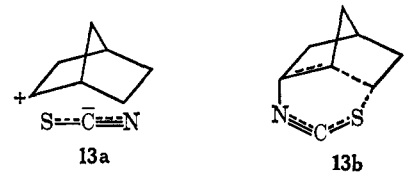


bear witness to the isomerization proceeding by dissociation–recombination. In addition, the lack of a special salt effect by perchlorate is a reflection of the absence of appreciable solvent-separated ion pairs during this process.[15] The striking effect of boron trifluoride on both rate and product distribution is also quite clear if attributed to its ability to coordinate with the thiocyanate group, nitrogen end. Collapse from a pair of this type (**12**) will occur with a sulfur–carbon bond being formed preferentially. The longer lifetimes



required for intermediates collapsing to give nitrogen–carbon bonds is clearly sufficient to eliminate the effects of coordinated ions analogous to **11a**. Thus it is not surprising that **4** is not detected under these conditions. Thiocyanate ion catalysis of isomerization was previously shown[4e] to proceed by a displacement process through use of isotopic labeling techniques. In our case the fact is experimentally more easily discerned by noting the sharp increase of uncyclized product **4**. It was fortuitous that under the conditions we utilized (see Table II) the two modes of isomerization were able to compete on about equal bases for **3**. Interestingly, this salt has no appreciable effect on the isomerization of **5** (due in all probability to the steric restrictions of the norbornyl skeleton). The **6**/**5** product ratio derived from **3** therefore remains unaffected by thiocyanate ion and confirms the remaining presence of the dissociation pathway.

Recently it has been pointed out by Collins and Lietzke[16] that a scheme of classical ions can be utilized successfully to explain the results from acetolysis of isotopically labeled 2-(Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (**1**).[8c] It was therefore of considerable interest to us to check for the presence of the *endo*-norbornyl derivatives **7** and **8** in the product mixture. The classical analog (**13a**) of ion **11a** could conceivably present a favorable means of obtaining *endo* attack,



thereby reinforcing this mechanistic suggestion. The alternate possibility of a competing cyclic process (**13b**) was also suspect. Absence, however, of any detectable *endo* products of isomerization effectively removes any conjecture favoring **13b**. The possibility of **13a** as an intermediate is weakened but not completely eliminated due to the known[17] strong preference of norbornyl cations for *exo* attack. We offer no further evidence in favor of a classical ion pathway for the π-route norbornyl mechanism. For reasons of simplicity, therefore, we have chosen to retain the bridged-ion notation.

Experimental Section[18]

2-(Δ^3-Cyclopentenyl)ethyl Thiocyanate (3). To 7.14 g (0.02 mole) of crude *p*-toluenesulfonate ester prepared from 3.3 g of 2-(Δ^3-cyclopentenyl)ethanol[7] was added 4.1 g of potassium thiocyanate dissolved in 30 ml of sulfolane and the mixture was heated at 70° for 15 hr. A 75-ml portion of water was added and the mixture was extracted with pentane. The extracts were dried and concentrated affording 3.82 g of crude thiocyanate. The crude material, shown by gc to be contaminated with approximately 4% of isothiocyanate **4** was added to a solution of 1.9 g (0.026 mole) of *n*-butylamine in 25 ml of dry dioxane and stirred for 18 hr. The mixture was then poured into 75 ml of water and extracted with pentane. The extracts were combined, dried, and concentrated. Distillation of the residue gave 2.78 g (68%) of product: bp 58–60° (0.1 mm); infrared spectrum (film), 3010, 2895, 2150, and 685 cm^{-1}; nmr (CCl_4), τ 4.36 (s), 7.03 (tr), 7.38–8.42 (mult).

Anal. Calcd for $C_8H_{11}NS$: C, 62.70; H, 7.24; N, 9.14; S, 20.93. Found: C, 64.93; H, 7.14; N, 9.17; S, 21.27[1]

(15) S. Winstein and D. Darwisch, *J. Am. Chem. Soc.*, **81**, 5511 (1959).

(16) C. J. Collins and M. H. Lietzke, *ibid.*, **89**, 6570 (1967).

(17) See J. A. Berson in "Molecular Rearrangments," Part 1, P. Demayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3, for a comprehensive survey.

(18) 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. Analyses were carried out by Micro-Analysis, Inc. of Wilmington, Del.

2-(Δ^3-Cyclopentenyl)ethyl Isothiocyanate (4). To a mixture of 1.2 ml of water and 0.6 ml of carbon disulfide being cooled in an ice–salt bath was added 0.813 g (0.007 mole) of crude amine prepared by reduction of 0.874 g of 2-(Δ^3-cyclopentenyl)acetamide.[19] A solution of 0.5 g of potassium hydroxide in 0.6 ml of water was added and the mixture was heated in a boiling-water bath for 25 min in a sealed tube. The mixture was cooled in an ice–salt bath, 0.72 g (0.07 mole) of ethyl chloroformate was added in one portion, and the solution was allowed to stand at room temperature for 1 hr. A solution of 0.4 g of potassium hydroxide in 0.6 ml of water was added and the reaction mixture was allowed to stand at room temperature for an additional 1 hr. The suspension was then extracted with ether, and the extracts were combined, dried, and concentrated. Distillation of the residue gave 0.710 g (64%) of product: bp 73–74° (0.6 mm); infrared spectrum (film), 3020, 2910, 1090, 1345, 1095, and 690 cm^{-1}; nmr (CCl_4), τ 4.44 (s), 6.50 (tr), 7.17–8.50 (mult).

Anal. Calcd for $C_8H_{11}NS$: C, 62.70; H, 7.24; N, 9.14. Found: C, 62.50; H, 7.25; N, 9.10.

1-(2^3-Δ-Cyclopentenylethyl)-3-*n*-butylthiourea Derivative of 4. A solution of 0.117 g (1.6 mmoles) of *n*-butylamine and 0.100 g (0.65 mmole) of **4** in 10 ml of dry dioxane was allowed to stand overnight. Water was added and the reaction mixture was extracted with ether and dried. The ether solution was concentrated to approximately 1 ml and cold pentane was added. An oil separated which crystallized when allowed to stand at −20°. The thiourea was recrystallized from ether–pentane giving white plates, mp 53.5–54.5°.

Anal. Calcd for $C_{12}H_{22}N_2S$: C, 63.66; H, 9.80; N, 12.37. Found: C, 63.63; H, 9.69; N, 12.38.

***exo*-2-Norbornyl Thiocyanate (5).** A solution of 3.6 g (0.036 mole) of potassium thiocyanate and 12.0 g (0.036 mole) of crude *endo*-2-norbornyl *p*-bromobenzenesulfonate,[9] in 40 ml of dry acetone was sealed in a glass tube and heated at 100° for 17 hr. The reaction mixture was poured into 100 ml of water and extracted with pentane. The extracts were dried and concentrated affording 4.573 g of crude product mixture. The crude material, shown by gc to contain 25% of isothiocyanate **6**, was separated by chromatography on silica gel and the thiocyanate distilled at 81–84° (1.9 mm) giving 2.06 g (37%) of colorless liquid: infrared spectrum (film), 2900, 2140, 1445, 950, and 760 cm^{-1}; nmr (CCl_4), τ 6.63 (oct), 7.53 (br s), 7.92–9.00 (mult).

Anal. Calcd for $C_8H_{11}NS$: C, 62.70; H, 7.24; N, 9.14; S, 20.93. Found: C, 62.51; H, 7.29; N, 9.18; S, 20.82.

***exo*-2-Norbornyl Isothiocyanate (6).** A 5.00-g (0.045 mole) portion of *exo*-2-norbornylamine[20] was subjected to the previously described procedure affording 5.01 g (72%) of product: bp 81–83° (2 mm); infrared spectrum (film), 2920, 2080, 1340, 945, and 760 cm^{-1}; nmr (CCl_4), τ 6.46 (tr), 7.57 (br s), 7.83–9.42 (mult).

Anal. Calcd for $C_8H_{11}NS$: C, 62.70; H, 7.24; N, 9.14. Found: C, 62.67; H, 7.20; N, 8.99.

1-(*exo*-2-Norbornyl)-3-*n*-butylthiourea. The derivative was prepared by the method previously described, affording white plates, mp 70–71°.

Anal. Calcd for $C_{12}H_{22}N_2S$: C, 63.66; H, 9.80; N, 12.37. Found: C, 63.71; H, 9.97; N, 12.12.

***endo*-2-Norbornyl Thiocyanate (7).** To 5 ml of a 2.7 *M* solution of cyanogen chloride in dry ether was added, dropwise, an ether solution of 0.252 g (0.002 mole) of 2-norbornylthiol (prepared from bicyclo[2.2.1]hept-2-en-5-yl thiolacetate[21]) and 0.410 g (0.004 mole) of triethylamine. The temperature was maintained at 10° during the addition. The mixture was then stirred for 19 hr, washed with water and saturated sodium bicarbonate solution, and dried. Concentration afforded 0.405 g of crude product which was distilled at 81° (2.25 mm) giving 0.115 g of a mixture. The mixture was shown by gc analysis to be 67% *endo*- (**7**) and 33% *exo*-2-norbornyl thiocyanate (**5**). The crude material was then dissolved in 5 ml of sulfolane and heated for 24 hr at 150°. At this time all of **5** had isomerized to **6**. The mixture was poured into 25 ml of water, extracted with pentane, dried, and concentrated. Treatment with *n*-butylamine as previously described and distillation afforded 0.040 g (14.2%) of pure **7**: infrared spectrum (film), 2900, 2140, 1445, 1172, 964, 950, and 768 cm^{-1}; nmr (CCl_4), τ 6.17 (mult), 7.43 (d), 7.67–9.17 (mult).

Anal. Calcd for $C_8H_{11}NS$: C, 62.70; H, 7.24. Found: C, 62.12; H, 7.25.

***endo*-2-Norbornyl Isothiocyanate (8).** A 6.65-g (0.045 mole) portion of commercial *endo*-2-norbornylamine hydrochloride was treated with sufficient potassium hydroxide to liberate the free amine and then subjected to the usual procedure giving 4.52 g (65%) of product, bp 78–82° (2.5 mm). The semisolid distillate was recrystallized from pentane affording a white solid: mp 38–41°; infrared spectrum (CCl_4), 2910, 2080, 1340, 884, and 750 cm^{-1}; nmr (CCl_4), τ 6.08 (mult), 7.67 (d), 8.48 (mult).

Anal. Calcd for $C_8H_{11}NS$: C, 62.70; H, 7.24; N, 9.14. Found: C, 62.47; H, 7.28; N, 8.97.

1-(*endo*-2-Norbornyl)-3-*n*-butylthiourea. The derivative was prepared by the method previously described affording white plates, mp 85–86°.

Anal. Calcd for $C_{12}H_{22}N_2S$: C, 63.66; H, 9.80 N, 12.37. Found: C, 63.68; H, 9.87; N, 12.40.

2-Cyclopentylethyl Thiocyanate (9). The sulfolane solution of 12.5 g (0.04 mole) of the crude *p*-toluenesulfonate ester, prepared from 2-cyclopentylethanol,[8a] was treated with 4.9 g (0.05 mole) of potassium thiocyanate in a procedure analogous to that used for **1**, The crude product was distilled, affording 4.5 g (60%) of product: bp 93–94° (5 mm); infrared spectrum (film), 2890, 2150, and 705 cm^{-1}; nmr (CCl_4), τ 7.08 (tr), 7.87–9.17 (mult).

Anal. Calcd for $C_8H_{13}NS$: C, 62.68; H, 7.29; N, 9.12. Found: C, 62.61; H, 7.28; N, 9.14.

2-Cyclopentylethyl Isothiocyanate (10). To a stirred suspension of 1.459 g (0.007 mole) of N,N′-dicyclohexylcarbodiimide and 7 ml of carbon disulfide in 40 ml of dry ether, being maintained at −10°, was added, dropwise, an ether solution of 0.766 g (0.007 mole) of 2-cyclohexylethylamine. When addition was completed the reaction mixture was stirred for 5 min at −10° and then the temperature was allowed to rise to room temperature. After 28 hr of stirring, the dicyclohexylthiourea was removed by filtration and washed with ether. Concentration of the combined filtrate and ether washings, followed by a distillation at 71–73° (1.0 mm) afforded 0.796 g (76%) of product which gc analysis showed to be contaminated with 5% of an impurity. A sample of 99.97% pure 2-cyclopentylethyl isothiocyanate was therefore gc collected and distilled at 68–69° (0.8 mm); infrared spectrum (film), 2910, 2100, 1445, 1345, 1090, and 688; nmr (CCl_4), τ 6.25 (tr), 7.72–9.14 (mult).

Anal. Calcd for $C_8H_{13}NS$: C, 61.88; H, 8.44; S, 20.65. Found: C, 61.61; H, 8.44; S, 20.51.

1-(2-Cyclopentylethyl)-3-*t*-butylthiourea. The derivative was prepared by the method previously described affording white plates, mp 86–87°.

Anal. Calcd for $C_{12}H_{24}N_2S$: C, 63.10; H, 10.59; S, 14.04. Found: C, 62.91; H, 10.70; S, 13.88.

Isomerization of 3 to 4, 5, and 6. Solutions 0.15, 0.015, or 1.5 *M* in pure **3** were prepared using tetramethylurea, acetonitrile, dimethylacetamide, dimethylformamide, or sulfolane. Aliquots (1 ml) were selated in glass tubes and heated at 150.0° for 24 hr. 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 solutions were washed twice with water, dried, and concentrated. The residues were examined by gc using the following columns and conditions: A, column, 10% Carbowax on Chromsorb W, 12 ft; temperature, 195°; carrier flow, 45 ml/min; retention time (min), **6** and **8**, 16.2; **4**, 18.0; **7**, 19.2; **5** and **10**, 20.6; **3**, 21.7; **9**, 25.0; B, column, 15% diethylene glycol succinate on Chromsorb W, 12 ft; temperature, 170°; carrier flow, 62 ml/min; retention time (min), **10**, 7.5; **6** and **8**, 10.2; **9**, 10.6; **4**, 12.2; **7**, 14.2; **5**, 15.8; **3**, 18.8.

Catalyzed Isomerization of 3 and 9 in Sulfolane. Aliquots (1 ml) of 0.1 *M* solutions of potassium thiocyanate and potassium perchlorate containing 0.15 *M* **3** and **9** were treated as previously described, and analyzed by gc using the same columns and conditions.

Catalyzed Isomerization of 3 in Benzene. A 0.015 *M* solution of **3** in benzene which was 0.3 *M* in boron trifluoride was heated under reflux. Samples (1 ml) were withdrawn at intervals of 14, 24, 45, and 95 hr. The samples were mixed with 5 ml of pentane, washed with a saturated solution of sodium bicarbonate, and dried. Upon concentration the samples were analyzed by gc in the usual manner.

Kinetic Procedure. Aliquots (5 ml) of sulfolane solutions 0.04 *M* in **3** were sealed in glass tubes and heated at 130.3 and 150.5°. Tubes were removed at various intervals and quenched by immersion in ice. The tubes were opened and the contents were poured

(19) S. J. Cristol and P. K. Freeman, *J. Am. Chem. Soc.*, **83**, 4427 (1961).

(20) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964).

(21) The thiolacetate was prepared by a Diels–Alder reaction of vinyl thiolacetate[11] and freshly distilled cyclopentadiene. The thiolester and double bond were reduced simultaneously with potassium azodicarboxylate.[22]

(22) J. Thiele, *Ann.*, **271**, 127 (1892).

into 20.0 ml of 0.021 *N* *n*-butylamine in dioxane. The mixtures were protected from moisture and allowed to stand overnight. The solutions were then titrated with 0.01 *N* HCl to the methyl red end point. A similar procedure was utlized for analysis of potassium perchlorate catalyzed isomerizations.

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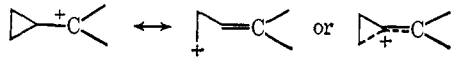
Carbonium Ion–Silane Hydride Transfer Reactions. III. Cyclopropylmethyl Cations

Francis A. Carey and Henry S. Tremper

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. *Received December 13, 1968*

Abstract: In methylene chloride–trifluoroacetic acid, cyclopropylcarbinols (**1a–e**) underwent rapid ring-opening reactions leading to 4-substituted 3-butenyl-1-trifluoroacetate esters (**2a–e**). With 1,1-dicyclopropylbenzyl alcohol (**1b**) and tricyclopropylcarbinol (**1c**), multiple ring opening occurred leading to bis- and tristrifluoroacetates **4** and **5**, respectively. With di- and triorganosilanes present in the reaction mixture, ring opening was suppressed and hydride transfer from ≡SiH to the carbonium ion took place, in several cases to the exclusion of ester formation. Hydride transfer produced cyclopropylmethanes (**3a–e**) exclusively and in no case was hydride transferred to a ring-opened homoallyl cation. This fact indicates that delocalization of the positive charge by the cyclopropyl ring takes place by some mechanism which does not make the ring carbons very electrophilic. The more highly substituted cyclopropylmethyl cations exhibit a greater tendency to ring open than the less substituted ones probably because of nonbonded repulsions in the ion. The stereochemical features of ring opening are discussed in terms of preferred conformations in the carbonium ion.

The reaction of silanes with carbonium ions produces alkanes by hydride transfer from silicon to carbon.[1,2] The primary products at silicon when trifluoroacetic acid is present are trifluoroacetoxysilanes[2] but these often undergo further reaction during work-up to afford silanols and disiloxanes. This transfer occurs readily under mild conditions and has been applied to carbonium ion studies as a nonnucleophilic irreversible trap for species such as the classical 2-phenylnorbornyl cation.[3] We were interested in observing if cyclopropylmethyl cations[4] could be trapped by silanes since the usual resonance description of these ions shows delocalization of positive charge into the three-membered ring and according to this description the possibility exists of hydride transfer to give cyclopropylmethanes and/or butenes.

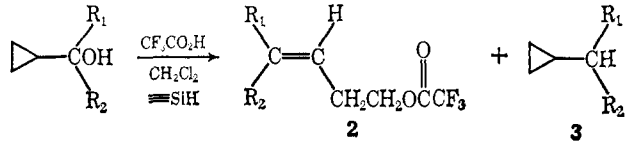


It seems reasonable that if hydride transfer from ≡SiH did occur that selection for attack at the ring methylene carbon or the cyclopropylcarbinyl carbon would bear some relationship to the electron deficiency at these positions and by examining several cyclopropylmethyl cations we could gain some insight into their structure.

(1) F. A. Carey and H. S. Tremper, *J. Amer. Chem. Soc.*, 90, 2578 (1968), and references cited there.
(2) D. N. Kursanov, Z. N. Parnes, G. I. Bassova, N. M. Loim, and V. I. Zdanovich, *Tetrahedron*, 23, 2235 (1967).
(3) F. A. Carey and H. S. Tremper, *J. Org. Chem.*, 34, 4 (1969).
(4) For reviews see: (a) M. Hanack and H.-J. Schneider, *Angew. Chem. Int. Ed. Engl.*, 6, 666 (1967); (b) S. Sarel, J. Yovell, and M. Sarel-Imber, *ibid.*, 7, 577 (1968); (c) N. C. Deno, *Progr. Phys. Org. Chem.*, 2, 129 (1964).

Results

The first carbonium ions examined were those which we thought would be the most stable and, therefore, the most likely to abstract hydride at rates competitive with ring opening. Cyclopropyldiphenylcarbinol (**1a**) when treated with trifluoroacetic acid in deuteriochloroform in an nmr tube underwent a very rapid reaction, complete in less than 1 min, to form 4,4-diphenyl-3-butenyl trifluoroacetate (**2a**) as the only detectable product. The structure was assigned on the basis of the characteristic nmr spectra of these types of esters.[5] For **2a–e** the signal for the vinyl proton appears in the region δ 4.8–6.8 coupled with the allylic methylene protons with a coupling constant of about 7 Hz. The signals for the protons in the $-CH_2OCOCF_3$ portion appear as a triplet in the region δ 4.2–4.5 and the allylic CH_2 signals as a symmetrical quartet at δ 2.3–2.8.



2 **3**

1a, $R_1 = R_2 =$ Ph
b, R_1 = Ph, $R_2 = c\text{-}C_3H_5$
c, $R_1 = R_2 = c\text{-}C_3H_5$
d, R_1 = Ph, R_2 = H
e, $R_1 = c\text{-}C_3H_5$, R_2 = H
f, $R_1, R_2 = (CH_2)_5$

When the trifluoroacetolysis was carried out on a preparative scale **2a** was isolated in 70% yield after distillation. Ring opening was suppressed, however,

(5) For spectra of related compounds see: (a) H. Hart and P. A. Law, *J. Amer. Chem. Soc.*, 86, 1957 (1964); (b) K. L. Servis and J. D. Roberts, *ibid.*, 87, 1331 (1965).