

# Solvolysis, Exchange, and Isomerization of 4,4'-Dimethylbenzhydryl Thiocyanate in 95% Aqueous Acetone<sup>1a,b</sup>

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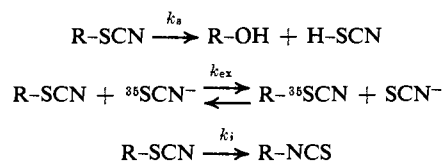
**Abstract:** In 95% aqueous acetone 4,4-dimethylbenzhydryl thiocyanate solvolyzes while it isomerizes. The solvolytic reaction displays common ion rate depression indicating that free carbonium ion intermediates are captured by the solvent. An analysis of the solvolytic and isotopic exchange rates,  $k_s$  and  $k_{ex}$ , with changing the concentration of the added common ion,  $SCN^-$ , shows that the sum  $k_s + k_{ex}$  remains constant and equal to the undepressed solvolytic rate,  $k_s^0$ . This finding demonstrates that the free carbonium ion is the only important intermediate involved both in the exchange and in the solvolysis process. The isomerization reaction is but slightly affected by the concentration of the common ion and appears to occur largely at a less advanced ionization stage, probably an intimate ion pair.

The ambident character of the  $SCN^-$  leaving group has been shown to be particularly suited to the study of ionization processes and return phenomena of neutral organic molecules.<sup>2</sup> In a recent paper evidence has been presented that the isotopic exchange accompanying the isomerization of the 4,4'-dimethylbenzhydryl thiocyanate in acetonitrile occurs at a more advanced stage of the ionization process than the intimate ion pair which is responsible, to the largest extent, of the isomerization.<sup>2b</sup> By studying the relative initial rates of radioactivity intake by the two isomers (thio- and isothiocyanate) and by knowing the first-order rate coefficient for the isotopic exchange, it was calculated that at 25° of 100 intimate ion pairs about 5 undergo exchange and 95 return to the covalent state thus setting to 5% the upper limit for the fraction of intimate ion pairs which dissociate.<sup>2b</sup> For a differently substituted substrate, the 4-chlorobenzhydryl thiocyanate, using a slightly different approach, the same limit was set to 2% in acetonitrile at 70°.<sup>2c</sup>

The data,<sup>2b,c</sup> however, did not provide any direct evidence about which particular intermediate was involved in exchange, the only indication being that the capturable species is one past the intimate ion pair stage. Even though it appeared likely that the intermediate is the free carbonium ion, this could not be ascertained since the only valid operational criterion for its involvement is the occurrence of the mass law effect.<sup>3</sup> We have undertaken the study of the kinetic behavior of 4,4'-dimethylbenzhydryl thiocyanate ( $R-SCN$ ) in 95% aqueous acetone, a solvolytic medium which might allow the

detection of mass law effect. The choice of this particular solvent mixture was based on the ionizing power which, judged from the rate of isomerization, is about the same as that of acetonitrile,  $8.60 \times 10^{-5}$  and  $8.97 \times 10^{-5} \text{ sec}^{-1}$  at 25°, respectively.

In this paper we report kinetic data on the solvolysis, isotopic exchange, and isomerization reactions.



Data are also given on the partition of radioactivity between thio- and isothiocyanate during isomerization and solvolysis.

## Results

In 95% aqueous acetone at 25°  $R-SCN$  solvolyzes while it isomerizes. When no electrolyte is present, acid and isothiocyanate are produced in the ratio 1 to 4 invariant with the per cent reaction, indicating that the alcohol and the isothiocyanate products are stable (see also Experimental Section). The rate of formation of acid fits quite well a first-order equation which provides the specific rate,  $k_{tot}$ , of disappearance of starting material,  $k_{tot} = k_s + k_i$ .<sup>4</sup> From  $k_{tot}$  and the product ratio  $[H^+]/[R-NCS]$ , the individual first-order rate constants for solvolysis,  $k_s$ , and for isomerization,  $k_i$ , were calculated. The linearity of the first-order plot (at least up to 85%) indicates the absence of common ion rate depression *within a run*. There may be three different reasons to account for this behavior: (a) the free carbonium ion is not involved as an intermediate<sup>3,5</sup>; (b) thiocyanic acid does not compete with water for the dissociated carbonium ion<sup>3</sup>; (c) the progressive slowing down of the first-order coefficient is exactly counter-

(1) (a) Abstracted in part from the doctoral thesis of I. P., University of Padova, 1962; (b) supported by Consiglio Nazionale delle Ricerche, Roma; (c) to whom inquiries are to be addressed: Istituto di Chimica Fisica, Padova, Italy.

(2) (a) A. Illiceto, A. Fava, U. Mazzuccato, and O. Rossetto, *J. Am. Chem. Soc.*, **83**, 2729 (1961); (b) A. Fava, A. Illiceto, A. Ceccon, and P. Koch, *ibid.*, **87**, 1045 (1965); (c) A. Fava, U. Tonellato, and L. Congiu, *Tetrahedron Lett.*, **22**, 1657 (1965); (d) L. A. Spurlock and P. E. Newallis, *ibid.*, **3**, 303 (1966); (e) L. A. Spurlock and T. E. Parks, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March 31–April 5, 1968, Abstract of papers, p 193; (f) for a review see A. Fava "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, New York, N. Y., 1966, p 73.

(3) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. G. Robinson, *J. Am. Chem. Soc.*, **78**, 328 (1956).

(4) In control runs the total rate was also obtained by following the appearance of isothiocyanate. The two methods gave identical results within experimental error.

(5) See ref 4 in ref 3.

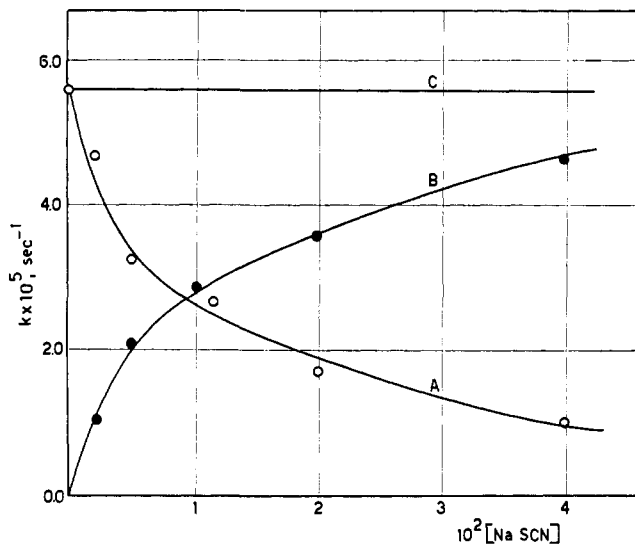


Figure 1. Plot of  $k_s$  (curve A),  $k_{ex}$  (curve B), and of the sum  $k_s + k_{ex}$  (curve C) as a function of NaSCN concentration (see Tables II and III).

acted by the increase of ionic strength during the course of the reaction.<sup>6</sup>

In order to make a choice among these possibilities, the salt effect was first determined. It turned out that in the presence of sodium perchlorate the ratio  $[H^+]/[R-NCS]$  while changing with changing  $NaClO_4$  concentration, remains constant within a given run, the rate of acid production giving an excellent fit for a first-order equation. The data for  $k_s$  and  $k_i$  are reported in Table I. The lack of common ion effect in these experiments

Table I. Salt Effect on the Rates of Solvolysis and Isomerization of 4,4'-Dimethylbenzhydryl Thiocyanate<sup>a</sup>

$[NaClO_4] \times 10^3, M$	$k_s \times 10^5, sec^{-1}$	$k_i \times 10^5, sec^{-1}$
	1.32	5.33
1.00	1.46	5.66
10.0	1.77	5.70
30.0	2.33	5.93
200	5.60	8.60

<sup>a</sup>  $[R-SCN] = 5 \times 10^{-2} M$ .

permits to rule out the possibility c above.

That the lack of mass law effect is due to inability of HNCS to compete with water for the carbonium ion was shown by an experiment carried out in the presence of *sym*-collidine (see Experimental Section). The first-order plot showed a large upward drift indicative of mass action. The effect of this bulky nonnucleophilic<sup>7</sup> base is to neutralize the acid produced during the course of the reaction. It appears that the collidine thiocyanate is dissociated enough to compete with water for the free carbonium ion while the acid is not. The study of the mass law effect was then approached by adding variable concentrations of sodium thiocyanate. To avoid all interferences from salt effects a saline buffer was used, 0.2 M total electrolyte adjusted with  $NaClO_4$ .

(6) M. G. Church, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 966 (1940).

(7) J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **79**, 2365 (1957).

Table II. First-Order Rate Constants for Solvolysis and Isomerization of 4,4'-Dimethylbenzhydryl Thiocyanate in 95% Aqueous Acetone at Constant Electrolyte Concentration<sup>a,b</sup>

$[NaSCN] \times 10^3, M$	$k_s \times 10^5, sec^{-1}$	$k_i \times 10^5, sec^{-1}$
	5.60	8.60
2.10	4.68	8.30
5.00	3.23	7.27
11.6	2.68	7.44
20.0	1.68	6.67
40.0	0.97	6.40

<sup>a</sup> Adjusted to 0.200 M with  $NaClO_4$ . <sup>b</sup>  $[R-SCN] = 5 \times 10^{-2} M$ .

The data are reported in Table II and plotted in Figure 1 (curve A). As the figure clearly indicates,  $k_s$  markedly decreases with increasing sodium thiocyanate the rate of decrease being higher in the low concentration region. At the higher NaSCN concentration employed 0.04 M solvolysis is 83% depressed.

In the presence of labeled (<sup>35</sup>S) sodium thiocyanate isotopic exchange also takes place. The rate of exchange<sup>8</sup> was measured at different NaSCN concentrations and the results given in Table III and plotted in

Table III. First-Order Rate Coefficients for Isotopic Exchange between 4,4'-Dimethylbenzhydryl Thiocyanate and NaSCN at Constant Electrolyte Concentration<sup>a,b</sup>

$[NaSCN] \times 10^3, M$	$k_{ex} \times 10^5, sec^{-1}$
2.20	1.00
5.04	2.08
10.3	2.88
20.1	3.56
40.0	4.65

<sup>a</sup> Adjusted at 0.2 M with  $NaClO_4$ . <sup>b</sup>  $[R-SCN] = 5 \times 10^{-2} M$ .

Figure 1 (curve B). The specific rate increases with NaSCN but the dependence is not linear. At the highest concentrations,  $k_{ex}$  approaches the rate of solvolysis measured in the absence of sodium thiocyanate,  $k_s^0$ . It is remarkable that at any concentration the sum  $k_s + k_{ex}$  is, within the experimental error, constant and equal to  $k_s^0$  (Figure 1, curve C).

#### Partition of Radioactivity between Thiocyanate and Isothiocyanate

If, as it is the case here, all radioactivity enters the organic substrates by way of ionization processes, one can evaluate the specific reactivities of the two ends of  $SCN^-$  vs. the carbonium ion. In fact, the ratio of the total number of labeled atoms which are found in the organic thiocyanate and on the isothiocyanate, extrapolated down to zero time, gives the mode of partition of the 4,4'-dimethylbenzhydryl cation in the covalent collapse. From this factor and from the rate constants of isomerization and exchange one can calculate the upper limit for the fraction of intimate ion pairs which ionize to the point to give exchange.<sup>2b</sup> We have carried out an experiment at  $[R-SCN] = 5 \times 10^{-2} M$  and  $[NaSCN] = 2 \times 10^{-2} M$  using a 0.2 M buffer electrolyte. The specific activities of the ionic thiocyanate, the organic thiocyanate and isothiocyanate were measured at

(8) Since R-SCN undergoes solvolysis and isomerization, the exchanging system is not a stable one. However, the rates of isomerization and solvolysis are slow enough to make the McKay plots linear up to 20-25% of exchange. Thus, the estimation at initial rates is quite accurate.

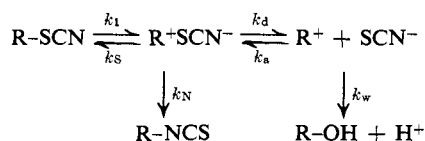
very small isomerizations, 2.7 and 3.2%. The ratio of total activities on thio and iso was found to be 8.3 in both experiments. This value corresponds to the partition factor between the sulfur and nitrogen ends.<sup>2b</sup>

### Discussion

It is clear from the data reported in Table I and Figure 1 that the solvolytic rate is depressed by the presence of common ion. This mass law effect is evidence of "external ion" return.<sup>3</sup> Furthermore the finding that the sum of the first-order specific rates for solvolysis and exchange is invariant with the concentration of the common ion and equal to the solvolytic rate which is observed in the absence of common ion, constitutes unequivocal evidence that solvolysis and exchange involve the same ionic intermediate which is the free carbonium ion. Independently of the presence of other ionic intermediates, if solvolysis and exchange occur at the carbonium ion level, the ratio of the solvolytic to the exchange rates must be a linear function of the concentration of the common ion. From this the competition factor can be derived between the solvent and the common ion. Figure 2 reports a plot of  $k_{ex}/k_s$  vs. NaSCN. The slope of the line is  $112 M^{-1}$  corresponding to a partition factor of 308 between  $SCN^-$  and  $H_2O$ . Accounting for the factor 8.2 between the sulfur and nitrogen ends of  $SCN^-$ , the relative rate factors for capturing the carbonium ion are 1, 33, and 275, respectively, for  $H_2O$ , the N and the S atom of  $SCN^-$ . These values fall within the range reported in the literature.<sup>9</sup> For example, for the same carbonium ion in 85% aqueous acetone a factor of 70 has been found between chloride ion and water.<sup>5</sup> It is reasonable that in this protic solvent chloride is intermediate between the nitrogen and sulfur ends of  $SCN^-$ .

The data allow the calculation of the fraction of intimate ion pairs which dissociate. The total rate of ionization,  $k_1$  (Scheme I), is given by  $k_1 = k_i(k_s/k_N + 1)$

### Scheme I



+  $k_s + k_{ex}$  and the fraction of ionic intermediates which dissociate is given by  $(k_{ex} + k_s)/k_1$ . Introducing the measured values of  $k_s/k_N$  and those of  $k_i$ ,  $k_{ex}$ , and  $k_s$  obtained under the same conditions, the above fraction is calculated to be 0.085. Thus of 100 ion pairs about 8.5 dissociate to carbonium ions while the rest collapse to covalent state in the ratio 8.3 to 1 thiocyanate to isothiocyanate.<sup>10</sup> Clearly then the fraction of isothiocyanate which is formed by way of free carbonium ions may reach 8.5% at most, that is when all the free carbonium ions are captured by thiocyanate. Therefore by far the largest fraction of isothiocyanate is formed at an ionization level prior the free carbonium ion.

(9) For reviews see (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 55; (b) C. A. Bunton, "Nucleophilic Substitution Reactions at a Saturated Carbon Atom," Elsevier Publishing Co., Amsterdam, 1963, p 140.

(10) This fraction 8.5% is very close to the value for the upper limit for the dissociation fraction found in acetonitrile (5.3%).<sup>2b</sup> It is then plausible to assume that also in the latter medium the exchange takes place at the dissociated carbonium ion level.

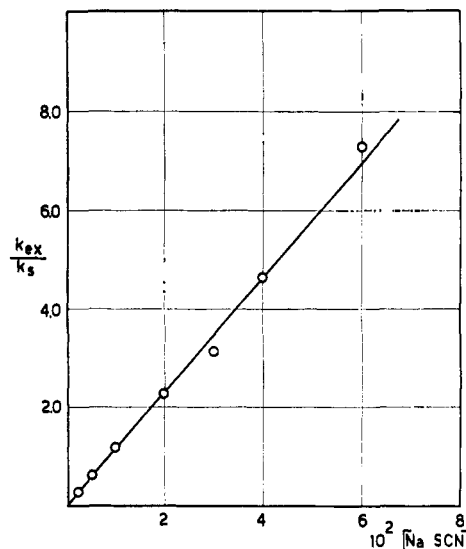


Figure 2. Plot of  $k_{ex}/k_s$  vs. NaSCN concentration.

This is consistent with the slight sensitivity to salt effect of the isomerization rate with respect to the solvolytic rate (see Table I).

All the data agree with the Scheme I and the discussion which has been presented here. There is, however, one discrepancy: this is the decrease of the isomerization rate with increasing NaSCN as illustrated in the last column of Table II. The obvious expectation would be exactly opposite since the isomerization rate should be increased though to a slight extent by that fraction of carbonium ions which is returned to isothiocyanate. In order to account for the observed decrease of the isomerization rate it would be necessary that either the ionization rate,  $k_1$ , decreases, or the  $k_s/k_N$  ratio increases. There is little ground at present to make any reasonable prediction on which factor it has been found that the  $k_s/k_N$  ratio, determined as above, is salt dependent. For example in acetonitrile the addition of 0.09 M  $NaClO_4$  increases the  $k_s/k_N$  value from 5.0<sup>2b</sup> to about 7.8.<sup>11</sup> In acetone the ratio is 4.2 with 0.001 M NaSCN, it increases to 6.7 upon addition of 0.099 M  $NaClO_4$ , and becomes 7.8 for NaSCN equal 0.02 M and  $[NaClO_4] = 0.08 M$ .<sup>11</sup>

While we are at present unable to account for these changes it is apparent that they may be responsible, at least in part, of the observed decrease of  $k_1$ .

### Experimental Section

**Solvent and Materials.** Commercial reagent grade acetone was refluxed over potassium permanganate and distilled. From redistillation over potassium carbonate, the fraction bp 56.4–56.5° was collected. Commercial reagent grade *sym*-collidine 99% was used without further purification. 4,4'-Dimethylbenzhydryl thiocyanate and isothiocyanate were reported previously.<sup>12</sup> Labeled sodium thiocyanate (<sup>35</sup>S) was prepared as previously described.<sup>13</sup> Sodium perchlorate and sodium thiocyanate were commercial reagent grade dried and stored over  $P_2O_5$ .

**Kinetics. Solvolysis and Isomerization.** Weighed amounts of organic thiocyanate were dissolved in an appropriate volume of acetone whereas the ionic reagents were dissolved in a mixture of

(11) I. Papa, unpublished.

(12) A. Ilceto, A. Fava, U. Mazzucato, and P. Radici, *Gazz. Chim. Ital.*, 90, 919 (1960).

(13) A. Fava and A. Ilceto, *Ric. Sci.*, 25, 54 (1955).

acetone-water to make up a final solution of 95% aqueous acetone v/v. The two solutions were put in the two arms of a Y-shaped reaction vessel and mixed at the desired temperature. For each run seven to ten samples (3–5 ml) were withdrawn at various time intervals to cover until 85% reaction. These aliquots were then added to benzene (5 ml) and the organic layer washed with water (by this procedure the thiocyanate is not solvolyzed appreciably). The aqueous solution was titrated for acid with standard aqueous sodium hydroxide.

The determination of isothiocyanate was carried out by reacting with excess piperidine. The amine reacts readily with the isothiocyanate to give quantitatively N-(4,4'-dimethylbenzhydryl)-N'-(cyclopentamethylene)thiourea, while the thio compound does not interfere. The excess amine was then titrated and the following procedure was used. Aliquots (2 ml) of the reacting solution were added to benzene (5 ml) and washed with water. The aqueous layer was extracted with 3-ml portions of benzene, the organic extracts were collected and the aqueous washing was discarded. A 0.1 M solution of piperidine (2 ml) in benzene was added and the solution allowed to stand for 30 min at room temperature. The benzene layer was extracted with 10 ml of 0.02 N HCl and water and the collected aqueous portions were titrated with 0.01 N NaOH. In some experiments the isothiocyanate was determined by ir. The wavelength was selected at 2050  $\text{cm}^{-1}$  corresponding to the absorption maximum for the isothiocyanate. A Perkin-Elmer Model 21 double beam instrument was used. The results were in good agreement with those obtained by titration. The product ratio [acid]/[R-NCS] did not change appreciably within a given run and this provides evidence for the stability both of the alcohol and the isothiocyanate under the reaction conditions. A solvolysis experiment carried out on 4,4'-dimethylbenzhydryl isothiocyanate confirmed this point. When the isothiocyanate ( $5 \times 10^{-2}$  M) was allowed to stand in 95% acetone with 0.2 M  $\text{NaClO}_4$  at 25° no appreciable formation of acid was detected after 48 hr corresponding to about ten half-lives for the thiocyanate.

Table IV

100f <sup>a</sup>	$A_{\text{NaSCN}}$	$A_{\text{R-NCS}}$	$A_{\text{R-SCN}}$	$A_{\text{R-SCN}}(1 - f)/A_{\text{R-NCS}}f$
2.75	950	81.0	19.0	8.30
3.20	930	77.3	21.3	8.35

<sup>a</sup> Fraction of isomerization;  $[\text{R-SCN}] = 5 \times 10^{-2}$  M;  $[\text{NaSCN}] = 2 \times 10^{-2}$  M;  $\text{NaClO}_4 + \text{NaSCN} = 0.2$  M; temperature = 25°.

The rate of formation of acid and isothiocyanate follows a first-order law with deviations which stay within 5% at least up to 85% reaction both in the absence and in the presence of salts ( $\text{NaClO}_4$  and/or  $\text{NaCN}$ ). A run carried out at  $\text{NaClO}_4 = 0.2$  M is reported in detail as follows (reaction, % ( $10^8 k_{\text{tot}}$ ,  $\text{sec}^{-1}$ ): 12.6 (15.0), 21.7 (13.6), 41.1 (14.8), 54.5 (14.6), 68.3 (14.7), 85.0 (14.7). On the contrary in an experiment carried out in the presence of 0.0486 M *sym*-collidine under the identical conditions the first-order rate coefficient showed a large decrease, as shown below (thiocyanate ion was determined by bromide titration): 17.7 (14.65), 31.4 (14.11), 44.3 (11.02), 52.9 (10.67), 59.4 (9.70).

**Exchange.** The same procedure for the preparation of the initial solution as that described for solvolysis runs was used. The work-up and the counting procedures have been described.<sup>2a</sup>

**Partition of Radioactivity between Thiocyanate and Isothiocyanate.** The detailed method has been previously described.<sup>2b</sup> The specific activities of the ionic thiocyanate,  $A_{\text{NaSCN}}$ , of the organic thiocyanate,  $A_{\text{R-SCN}}$ , and of the isothiocyanate,  $A_{\text{R-NCS}}$ , which have been observed at 2% isomerization are reported in Table IV. The specific activities are expressed in arbitrary units, having set  $A_{\text{NaSCN}} = 1000$  at time zero. In the last column the ratio of total activities on the two species R-SCN and R-NCS is given.

## Memory Effects in Multiple Carbonium Ion Rearrangements. I. The Ring-Expansion Route to Cations of the Bicyclo[2.2.2]octenyl Series<sup>1</sup>

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**Abstract:** Ring expansions of 2-norbornenyl-*syn*-7-carbinyl substrates in a variety of carbonium ion reactions lead to twice-rearranged products *via* intermediates different from those generated from the *anti* isomers. The major products from the *syn* system are in the G series previously encountered by Goering in solvolyses of bicyclo[2.2.2]-oct-5-en-2-*endo*-yl derivatives, whereas those from the *anti* system give mainly products (L series) observed by LeBel from bicyclo[2.2.2]oct-5-en-2-*exo*-yl derivatives. The specificity of the second rearrangement step is not perfect, however, and some "memory" is lost by crossover from the *syn* system to the L series and from the *anti* system to the G series. The product-forming twice-rearranged cations show all the characteristics of the typical G and L intermediates, but the latter two cations when generated from bicyclo[2.2.2]oct-5-en-2-yl substrates do not cross over appreciably. An extra intermediate or reaction path permitting crossover therefore must be inserted in the mechanism for the ring expansions. This intermediate is not efficiently trapped by external nucleophiles. Environmental factors such as solvent, ionic concentration, electrophilic catalysts, and variation of the leaving counterion have remarkably little effect on the selectivities of the second rearrangement step.

In the ring-expansion route to bicyclic carbonium ions, the nature of the product-forming intermediates depends markedly upon the stereochemistry of the

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(2) (a) Please address inquiries to this author at Sterling Chemistry Laboratory, Yale University, New Haven, Conn. 06520. (b) Dow Chemical Co. Fellow, 1964–1965.

reactant. The prototypical cases are derived from the *endo*- and *exo*-2-norbornylcarbinyl systems (1 and 2), which give two distinctively different intermediates. It is both plausible and convenient to refer to these as the conformationally isomeric chair and boat cyclohexyl cations 3 and 4.<sup>3</sup> Whether this is the only possible

(3) (a) J. A. Berson and P. Reynolds-Warnhoff, *J. Am. Chem. Soc.*, **84**, 682 (1962); **86**, 595 (1964); (b) J. A. Berson and D. Willner, *ibid.*, **84**, 675 (1962); **86**, 609 (1964).