The Nature of the Carbonium Ion. VI. The *anti*-7-Norbornenyl and 7-Norbornadienyl Cations from Thiocyanate Isomerizations

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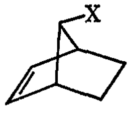
Received August 5, 1970

The thermal isomerizations of *anti*-7-norbornenyl (**7**) and 7-norbornadienyl (**11**) thiocyanates were investigated in various polar aprotic solvents. Both compounds gave isothiocyanates of retained structure only (**8** and **12**, respectively), despite special attention to the isolation of tricyclic products. Rates of isomerization were measured and activation parameters calculated. The reactions used in preparation of **7** and **11** and the effects of potassium thiocyanate, lithium perchlorate, and tetramethylammonium azide on the isomerizations were utilized to explain the unexpected inability of the thiocyanate ion to give tricyclic products from the cationic intermediates.

In this paper, we describe the results from studies of ionization at the C_7 positions of norbornyl and norbornadienyl skeleta[3] utilizing the thiocyanate–isothiocyanate isomerization technique[4] for the examination of ion pairs. In other papers of this series[5] we have shown that only those primary and secondary sites which receive appreciable intramolecular assistance from an internal nucleophile (including resonance stabilization) are capable of supporting the isomerization of alkyl thiocyanates. As the anti C_7-substituted norbornenyl and the C_7-substituted norbornadienyl derivatives seemed quite qualified to meet this criterion,[6] they were logical choices for further study of ion-pair behavior and the influences of structure on thiocyanate reactivity.



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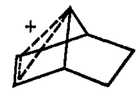

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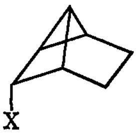

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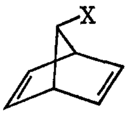

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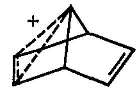

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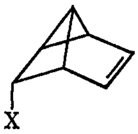

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It was assumed that the very stable "bishomocyclopropenyl" cations, **2** and **5**, which contribute to solvolytic reactivities of **1** OTs[7] and **4** Cl,[8] respectively, would contribute similarly to isomerization. These compounds were interesting also because of more work by Winstein[9a] and by Tufariello[9b] which showed that upon neutral hydrolyses of *anti*-7-norbornenyl *p*-toluenesulfonate or benzoates **1** (X = OTs, OPNB, OPMB) there is quantitative conversion *via* ion **2** to alcohol of retained structure with no indication of *endo*-tricyclo[3.2.0.0^{2,7}]heptan-6-ol (**3** OH) found. This occurred despite the stability of the latter to reaction conditions; thus it was concluded that **1** OH must be the product of kinetic control. Since the corresponding thiocyanate isomerization must proceed through ion pairs with cations resembling **2**, it was of interest to determine if the ions of isomerization showed similar behavior with regard to structural preference. Whether stable tricyclic products could be obtained by this method was not clear; however, it did seem possible on the bases of the high nucleophilicity of thiocyanate ion and reports[9,10] which indicated that with sufficiently strong nucleophiles cation **2** could be attacked appreciably at the endo C_2–C_3 face as well as at C_7.

Most of these same questions were also pertinent to the 7-norbornadienyl analog since cation **5** had been shown[10] to undergo similar behavior in the presence of very good nucleophiles. We therefore synthesized 7-norbornadienyl thiocyanate (**11**) and isothiocyanate (**12**), as well *anti*-7-norbornenyl thiocyanate (**7**) and isothiocyanate (**8**), in order to explore these problems.

Results

anti-7-Norbornenyl thiocyanate (**7**) and isothiocyanate (**8**) were prepared from the known[7] *anti*-7-norbornenyl *p*-toluenesulfonate (**1** OTs). Treatment of the sulfonate ester with potassium thiocyanate in dimethylformamide or sulfolane gave a mixture consisting of **7** and **8** in a 75:25 ratio[11] (Scheme I). The separation of this mixture by chromatography on silica

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[2] From the thesis submitted by Y. Mikuriya in fulfillment of the requirements for the M.S. Degree, Temple University, 1969.

[3] For a review of the pertinent ionic reactions of these skeleta, see J. A. Berson in "Molecular Rearrangements," part 1, P. de Mayo, Ed., Interscience, New York, N. Y., Chapter 3.

[4] For recent reviews, see L. A. Spurlock and T. E. Parks in "Mechanisms of Reactions of Sulfur Compounds," Vol. 3, N. Kharasch, Ed., Intra-Science Research Foundation, Santa Monica, Calif.; A. Fava in "Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, Oxford, England, p 73.

[5] (a) L. A. Spurlock and W. G. Cox, *J. Amer. Chem. Soc.*, **91**, 2961 (1969); (b) L. A. Spurlock and T. E. Parks, *ibid.*, **92**, 1279 (1970); (c) L. A. Spurlock and R. J. Schultz, *ibid.*, **92**, 6302 (1970); (d) L. A. Spurlock and W. G. Cox, *ibid.*, **93**, 146 (1971).

[6] The *syn*-7-norbornenyl position was briefly considered for this study. It was observed, however, that the corresponding *p*-toluenesulfonate solvolyzed 54,000 times slower than cyclohexyl *p*-toluenesulfonate. Since cyclohexyl thiocyanate could not be made to isomerize, presumably due to insufficient stability of the cation, there was negligible likelihood that *syn*-7-norbornenyl thiocyanate would behave differently. Isomerization of this compound was therefore not attempted.

[7] S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, **77**, 4183 (1955); S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

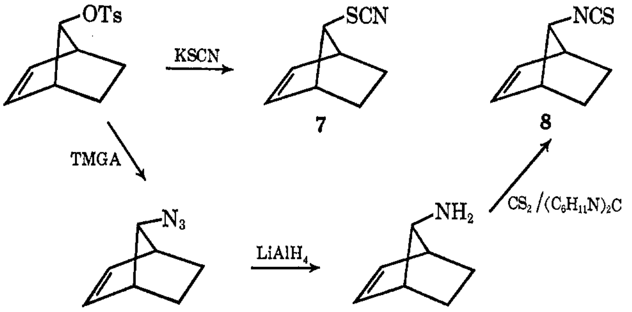
[8] S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

[9] (a) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966); (b) J. J. Tufariello, T. F. Mich, and R. J. Lorence, *Chem. Commun.*, 1202 (1967); (c) J. Lhomme, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 1548 (1969); (d) J. J. Tufariello and R. J. Lorence, *ibid.*, **91**, 1546 (1969).

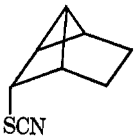
[10] S. Winstein, A. Lewin, and K. Pande, *ibid.*, **85**, 2324 (1963); H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); H. Tanida, T. Tsuji, and T. Irie, *ibid.*, **88**, 864 (1966); H. Tanida and T. Hata, *J. Org. Chem.*, **30**, 977 (1965).

[11] The fact that this mixture was obtained constitutes a support of structural assignment in itself since a displacement reaction, giving *syn* product, would be expected to produce almost exclusively thiocyanate product. See A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Amer. Chem. Soc.*, **87**, 1045 (1965).

SCHEME I



gel gave pure **7**, whose infrared spectrum showed a sharp absorption at 2150 cm^{-1} characteristic of the alkyl thiocyanate group, and pure **8**, which showed the broad intense absorption between 2160 and 2070 cm^{-1} typical of isothiocyanates. Addition of *n*-butylamine to the crude mixture of **7** and **8** also gave pure thiocyanate after distillation, while **8** reacted to give the crystalline 1-*n*-butyl-3-(*anti*-7-norbornenyl)thiourea. Analyses by nmr and gc of the crude mixture, purified **7** and **8**, and the thiourea indicated that neither tricyclic compound **9** or **10** had been formed. For further confirmation of structure, **1** OTs was allowed to react with tetramethylguanidinium azide.[12] The resultant *anti*-7-norbornenyl azide was then reduced to the corresponding amine which was subjected to a conventional[5a] preparation of isothiocyanates (Scheme I). The product obtained and its *n*-butylthiourea derivative were identical with the minor component and its derivative from the treatment of **1** OTs with thiocyanate ion. Interestingly, despite attempts to provide as low temperatures as were feasible for the preparative reactions, and the employing of various excesses (tenfold maximum) of the nucleophiles, SCN$^-$ and N$_3^-$, no appearances of tricyclic products were detectable. The compositions of **7** and **8** were further authenticated by elemental analyses.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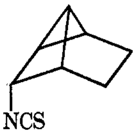
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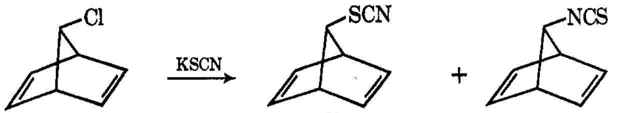
A mixture of 7-norbornadienyl thiocyanate (**11**) and isothiocyanate (**12**) was obtained by the reaction of potassium thiocyanate with 7-norbornadienyl chloride[8] in acetone. Gc and nmr analyses revealed a 95:5 ratio of thiocyanate to isothiocyanate. These rather unstable compounds (a sample of the crude mixture turned to a semisolid white polymer after 1 week at −20°) could be separated only by the aforementioned amine treatment. Pure thiocyanate **11** was obtained in this fashion along with crystalline 1-*tert*-butyl-3-(7-norbornadienyl)thiourea (from *tert*-butylamine). Due to the instability of 7-norbornadienyl azide, an authentic sample of isothiocyanate **12**, free of **11**, was obtainable only by heating **11** at 80° for several hours in acetonitrile. This material and its *tert*-butylthiourea derivative were identical by infrared, nmr, and gc analyses to the product from 7-norbornadienyl chloride and its thiourea derivative, respectively. The proper elemental analyses were also obtained for these compounds. As before, no tricyclic compounds (such as **13** or **14**) were to be found.

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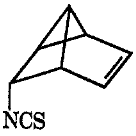
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The isomerizations of **7** were carried out in sulfolane dimethylformamide, acetonitrile, and tetramethylurea. Effects of salts on isomerization were studied by the addition of potassium thiocyanate or lithium perchlorate to solutions of **7**, in sulfolane only, since it was apparent that this was the most efficient solvent for isomerization and gave the cleanest results. Material recovery from all solvents was never less than 95%. Identification of isomerization products and measurements of remaining thiocyanate **7** at various time intervals were carried out by nmr and by gc. The identity of the single isomerization product with **8** was confirmed by a comparison of nmr spectra and gc retention times on three columns of different liquid phases.

Isomerizations of 7-norbornadienyl thiocyanate (**11**) could be reliably effected only in acetonitrile and at lower temperatures than used for **7** due to the extreme reactivity and limited stability of the diene–thiocyanate. Potassium thiocyanate was the only salt utilized for study of the effects of added ionic substances. Even at the lowest temperature reasonable for the isomerization, the only identifiable product was the isothiocyanate of retained structure **12**. The methods of analysis were analogous to those employed for isomerizations of **7**.

Since for both **7** and **11** no tricyclic products were detected, the possibility of an equilibration process was suspected. This had precedent as it had been observed[13] that an equilibrium exists between furfuryl thiocyanate and isothiocyanate in these same solvents. Because the efficiency of this equilibration was apparently related to the extreme stability of the furfuryl cation, it seemed possible that the stabilities of the cations from **7** and **11** might also lead to this result. The isomerization of **7** was therefore carefully followed at 80 and 110° by nmr analyses of aliquots taken at short intervals. Ultimately the spectra showed the complete disappearance of **7** and only the appearance of **8** in every case. Gc examinations confirmed this result to the limits of detectability (<0.1%). Similar experiments beginning with pure isothiocyanate **8** showed neither the additional presence of **7** nor any other species after 2 days. While this does not rule out the ionization of **8**, it does confirm the fact that like most isomerizing alkyl systems[2] the equilibrium position lies far to the side of the isothiocyanate. A further examination of the isothiocyanate ionization

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[12] A. J. Papa, *J. Org. Chem.*, **31**, 1426 (1966).

[13] L. A. Spurlock and R. G. Fayter, *ibid.*, **34**, 4035 (1969).

question was effected by adding five- and tenfold molar excesses of tetraethylammonium azide, first to sulfolane solutions of **7** (and **11**) and then to solutions of **8**. After heating at 80 or 110°, much tar was formed in the thiocyanate solutions but nearly none in the isothiocyanate solutions. Gc analysis of the products from the thiocyanates revealed only the presence of the corresponding azides, while **8** was solely detectable in the isothiocyanate samples. An attempt to improve the quantitative aspects of this observation by utilization of tetraethylammonium bromide failed due to the inability of bromide ion to compete successfully with thiocyanate ion for the intermediate cations. On the basis of the azide results, we therefore concluded that ionization of **8** probably does not occur to any appreciable extent and is therefore unimportant to the overall reaction.

The first-order rate constants for isomerizations of **7** and **11**, followed by gc, were determined graphically from plots of log [relative mole fraction RSCN] *vs.* time. Activation parameters were calculated where appropriate. The results, which are the averages of at least two runs, are tabulated in Table I. The reactions were followed to 50–70% completion depending on the rates of decomposition by starting material and product in the particular solvent.

TABLE I

RATE DATA FOR ISOMERIZATIONS OF **7** AND **11**

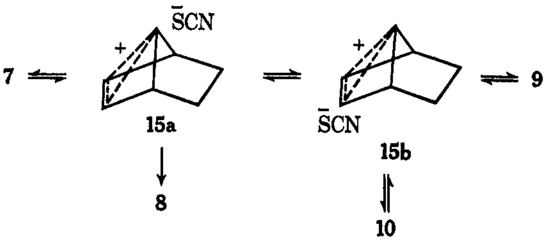
Solvent	Salt, *M*	*T*, °C	10^5k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
		7			
Sulfolane		81.0	0.44 ± 0.01		
		111.0	8.45 ± 0.25	26	−8
	KSCN (0.2)	110.0	9.68 ± 0.36		
	$LiClO_4$ (0.1)	110.0	13.2 ± 0.05		
CH_3CN		111.0	2.32 ± 0.02	26	−13
		130.5	13.0 ± 0.2		
DMF[a]		110.0	3.94 ± 0.20		
TMU[a]		110.0	0.24 ± 0.02		
		11			
CH_3CN		59.2	1.16 ± 0.02		
		81.5	12.5 ± 0.2		
		110.0	185[b]	25	−5[b]
	KSCN (0.5)	79.0	16.7 ± 0.2		

[a] DMF = dimethylformamide; TMU = tetramethylurea. [b] Extrapolated from data at other temperatures.

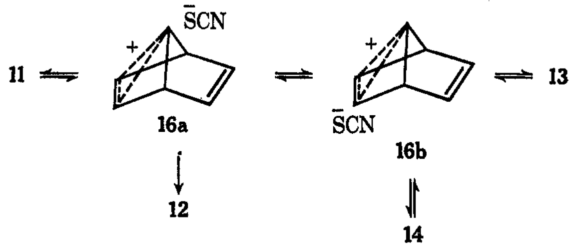
Discussion

The very facile isomerizations of **7** and **11**, and the strong solvent dependence of the rates, bore out our original hopes that these compounds would isomerize *via* the ionic routes typical[4,5] of many other nonallylic alkyl thiocyanates. These are in fact the most rapidly isomerizing alkyl thiocyanates which we have encountered and, excepting some substituted benzhydryl[14] isomerizations, are the most reactive ionic thiocyanate conversions yet measured. This strongly implies that the ion pairs formed from **7** and **11** may resemble at least **15a** and **16a**, respectively (Schemes II and III), if the analogies to solvolytic intermediates and to the norbornyl isomerizations[5a,b] hold. Even the initially surprising compression of the rates of these thiocyanates (k_7/k_{11} = 80), when compared with solvolytic results from the chlorides (k_{1Cl}/k_{4Cl} = 1000), becomes understandable if one considers that the transition state for isomerization probably involves tighter bonding between carbonium ion and leaving group.[4] The one plausible alternate pathway to isomerization, direct displacement by thiocyanate ion, can be eliminated by failure, even in large excesses of the ion, to find any *syn*-7-norbornenyl products of back-side attack on **7**. Two problems therefore present themselves: (1) to what degree of dissociation the ions proceed, and (2) the reasons for the absence of tricyclic products.

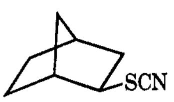
SCHEME II



SCHEME III



The formation of *anti*-7-norbornenyl azide and 7-norbornadienyl azide from treatment of isomerizing solutions of **7** and **11** with large azide ion excesses showed some indication that dissociation past the intimate pair must take place.[15] It was unfortunate that the stabilities of the azides, and the insufficient nucleophilicity of bromide ion, did not allow quantitative estimates of this effect. Since these same problems were encountered in our studies of *exo*-2-norbornyl thiocyanate (**17**) and ultimately resolved by use of rather involved isotopic labeling experiments,[5b] we preferred to draw conclusions by analogies to this isomerizing system and the similarly studied[16] 4,4′-dimethylbenzhydryl thiocyanate (**18**). In the case of **7** the rate of isomerization at 81.0° in sulfolane (Table I) is identical with that of **17** in the same solvent at 130.0° ($k_1 = 0.43 \times 10^{-5}$ sec^{-1}). Estimations, based on the amount of incorporation of ^{35}S-labeled thiocyanate ion into the product and starting



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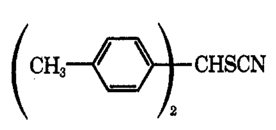

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[14] The rate of isomerization of **11** at 81.5° is about four times greater than that reported for benzhydryl thiocyanate at 70° in the same solvent: A. Iliceto, A. Fava, U. Mazzucato, and O. Rosetto, *J. Amer. Chem. Soc.*, **83**, 2729 (1961).

[15] Ionic strengths of these solutions were admittedly greater than those of the uncatalyzed isomerizations but were at least equivalent to those reactions where potassium thiocyanate demonstrated only minor effects on the isomerization.

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

material at this temperature and a RSCN/RNCS ratio of 2 for attack by the two ends of thiocyanate on the carbonium ion, lead to the conclusion that approximately 88% of the intermediates from **17** dissociate no further than the intimate pairs.[5b] Lacking the exchange data for **7**, but utilizing the known RSCN/RNCS = 3 value and the isomerization rate, we have assumed[17a] the rate of ionization to be about one-third higher than that for **17** and calculate[17b] that a *minimum* of 16% of the intimate ion pairs from **7** dissociate further in sulfolane at 81°. A similar treatment of **11** gives an estimate of 37% dissociation past the intimate stage during isomerization at 81.5°. These observations lend support to the notion that the failure to observe tricyclic products may be at least partially the result of thermodynamic favoring of the 7-norbornenyl and 7-norbornadienyl skeleta rather than solely the failure of ions like **15a** and **16a** to change the relative positions of nucleophile and carbonium ions to those indicated in **15b** and **16b**.

The most conclusive evidence in this behalf is the inability to observe tricyclic products from the preparative reactions with thiocyanate ion and **1** OTs or **4** Cl. As great care was taken to preserve the structural integrity of the products, and conditions were utilized where a lesser nucleophile (CN^-) does lead to tricyclic materials,[10] it seems safe to conclude that these must revert to norbornenyl and norbornadienyl compounds very rapidly.[18] Support for this comes from recent reports[9c,d] that the tricyclic-substituted benzoate esters **3** OPNB and **3** OPMB solvolyze 10^{10}–10^{12} times faster than their *anti*-7-norbornenyl counterparts. The lack of tricyclic products in the isomerization mixtures may then be the result of conditions too drastic to isolate them.

The nature of cationic mobility relative to the thiocyanate ion remains only partly defined by these observations due to the extreme instabilities of the tricyclic skeleta relative to the bicyclic ones. As a consequence, in the succeeding paper[5d] of this series we turned to the 5-norbornenyl cations where the situation is clarified by the thermodynamic favoring of the nortricyclyl skeleton over its bicyclic counterpart.

Experimental Section[19]

***anti*-7-Norbornenyl *p*-Toluenesulfonate (1 OTs).**—To a solution of 1.10 g (0.01 mol) of *anti*-7-norborneol[20] (**1** OH) in 2.5 ml of pyridine being stirred at 5° was added dropwise a solution of 2.80 g (0.015 mol) of *p*-toluenesulfonyl chloride in 3 ml of pyridine. During addition, the temperature of the mixture was kept between 5 and 10°. The mixture was stirred for 2 hr at 10° and then kept in the refrigerator overnight. It was poured into 30 ml of ice water and extracted with a 50% ether–pentane solution. The combined extracts were washed first with iced 10% hydrochloric acid, then saturated sodium carbonate solution, and dried over magnesium sulfate. The solvent was evaporated affording 2.51 g (95%) of pinkish white crystalline **1** OTs. The crude product was used immediately since it decomposed within a few hours at room temperature; ir (Nujol mull) 2900, 1370, 1180, 1190, 950, and 870 cm^{-1} was obtained.

***anti*-7-Norbornenyl Thio- (7) and Isothiocyanate (8).**—To a solution of 8.0 g (0.03 mol) of crude **1** OTs in 400 ml of distilled dimethylformamide was added 32.0 g (0.3 mol) of potassium thiocyanate. The mixture was stirred at room temperature for 65 hr. It was poured into 400 ml of water and extracted with pentane. The combined extracts were washed with water and dried over magnesium sulfate. The solvent was evaporated and the distillation of the crude product gave 3.3 g (73%) of a mixture of **7** and **8**: bp 54–60° (0.08 mm); ir (film) 3000, 2220, 2180, 2100, 1560, 1320, 750, and 710 cm^{-1}; nmr (CCl_4) τ 8.8 (multiplet), 8.1 (multiplet), 7.1 (multiplet), 4.05 (triplet). The gc analysis (LAC-728) showed a 75:25 ratio of **7** to **8**.

***anti*-7-Norbornenyl Thiocyanate (7).**—The following methods were employed for the isolation of **7** from the mixture.

Method A.—To a solution of 1.85 g (0.025 mol) of *n*-butylamine dissolved in 55 ml of purified dry dioxane was added 3.31 g of the mixture of **7** and **8**. The solution was stirred at room temperature for 5 hr. It was then poured into ice water and extracted with pentane. During the extraction, *anti*-7-norbornenyl-*n*-butylthiourea precipitated out necessitating filtration before separating the layers. The combined extracts were washed with ice-cold 10% hydrochloric acid, then saturated sodium bicarbonate, and dried over magnesium sulfate. The solvent was evaporated and distillation of the crude product afforded 1.70 g of **7**: bp 28–30° (0.07 mm); ir (film) 2950, 2180, 1275, 815, and 800 cm^{-1}; nmr ($CDCl_3$) τ 8.8 (multiplet), 8.05 (multiplet), 7.0 (quartet), 6.6 (triplet), 3.8 (triplet).

Anal. Calcd for C_8H_9NS: C, 63.59; H, 5.96; N, 9.27. Found: C, 63.41; H, 6.23; N, 9.23.

1-(*anti*-7-Norbornenyl)-3-*n*-butylthiourea, obtained as a by-product above, was recrystallized from ether–pentane, mp 84.0–85.0°.

Anal. Calcd for $C_{12}H_{20}N_2S$: C, 64.22; H, 8.98; N, 12.49. Found: C, 64.21; H, 8.82; N, 12.55.

Method B.—A 7.46-g (0.049 mol) portion of the mixture of **7** and **8** was chromatographed on 400 g of silica gel. **8** (1.47 g) was eluted with pentane and distilled: bp 75.0° (3 mm); ir (film) 2930, 2200, 2100, 790, and 775 cm^{-1}. Continued elution with ether gave 5.81 g of **7**: bp 60.0–65.0° (1.0 mm); ir (film) 2950, 2150, 1280, 815, and 805 cm^{-1}.

Tetramethylguanidinium azide was prepared by the procedure described by Papa.[12] The hygroscopic product was kept in a vacuum desiccator.

***anti*-7-Norbornenyl Azide.**—To 15.0 g (95 mmol) of tetramethylguanidinium azide dissolved in 200 ml of chloroform was added a solution of 2.50 g (9.5 mmol) of **1** OTs in 8 ml of chloroform. Addition took place over a period of 10 min. The mixture was then stirred at room temperature for 15 min and allowed to stand for 20 hr. The solution was concentrated and 200 ml of ether was added. A precipitate formed and was removed by filtration and washed with ether. Evaporation of the filtrate yielded 1.47 g (100%) of the crude azide: ir (film) 2950, 2100, 1370, 1330, 1180 and 1190 cm^{-1}.

***anti*-7-Norbornenyl Amine.**—To a solution of 0.84 g (0.022 mol) of lithium aluminum hydride in 40 ml of ether being stirred at room temperature was added a solution of 1.46 g (0.011 mol) of the crude azide in 20 ml of ether over a period of 30 min. The mixture was stirred at room temperature for 66 hr and then were added 0.84 ml of water followed by 2.5 ml of 15% potassium hydroxide and finally 0.84 ml of water. The precipitate was removed by filtration and washed with ether, and the combined filtrate and washings were dried over magnesium sulfate. Evaporation of the solvent afforded 0.88 g (75%) of the crude amine. A further purification was not attempted; ir (film) 3300, 2900, 1630, 1120, and 1050 cm^{-1} was obtained.

***anti*-7-Norbornenyl Isothiocyanate (8).**—To a solution of 1.68 g (8.1 mmol) of *N*,*N*′-dicyclohexylcarbodiimide and 3.2 ml of

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[17] (a) The relationship[5b] used to estimate the ionization rate (k_i) was $k_i = (k_S + k_N/k_N)k_t$. (b) Assuming also that the ionization rate and exchange rate are related similarly ($k_i \approx k_{ex}$) for **7** and **17** (as they are for **17** and **18**) the following equation, employing the isomerization rate (k_t) and RSCN–RNCS ratio (k_S/k_N), was used for calculation: $k_{ex}k_N/k_t\,(k_S + k_N)$ = *fraction of dissociated ion pairs.*

[18] The isomerization rates of the isothiocyanates, **10** and **14**, must indeed be spectacular since they clearly would exceed by many powers of ten that of furfuryl isothiocyanate, the only other ionically isomerizing isothiocyanate on which has been observed any measurable rate.[13]

[19] Melting points and boiling points were uncorrected. *Infrared spectra* were obtained on a Perkin-Elmer Infracord Model 137B using sodium chloride optics. Nmr determinations were carried out on a Varian Associates A-60A spectrometer. An F & M gas chromatograph (Model 700) was employed for analyses and kinetics using 2 ft × 0.25 in. columns. Packing materials were 15% diethylene glycol succinate on 70–80 mesh Chromosorb W (LAC 728) and 20% fluorosilicone (FS-1265) on 70–80 mesh Chromosorb W (QF-1). Organic solvents were of ACS reagent grade unless otherwise stated. Sulfolane was treated with potassium permanganate and distilled under vacuum. Dimethylformamide was distilled from calcium hydride and acetone from potassium permanganate. Elemental analyses were performed by Micro-Analysis, Inc., Wilmington, Del.

[20] B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965).

carbon disulfide in 17 ml of ether was added 0.88 g (8.1 mmol) of crude amine dropwise at −10°. The mixture was stirred and the temperature was allowed to rise to 20° over a period of 3 hr. The stirring was continued for 18 hr. The mixture was then filtered and the residue was washed with ether. Evaporation of the solvent followed by distillation of the residue gave 0.31 g of **8** which was slightly contaminated with *N,N'*-dicyclohexylcarbodiimide, bp 37–80° (0.5–0.1 mm). The product was purified by gc collection (2 ft × 0.25 in. LAC 728) and further by distillation: bp 34.0° (0.08–0.06 mm); ir (film) 2900, 2160, 2070, and 775 cm^{-1}; nmr (CCl_4) τ 8.3 (multiplet), 6.9 (quartet), 6.45 (singlet), 3.6 (triplet).

Anal. Calcd for C_8H_9NS: C, 63.59; H, 5.96; N, 9.27. Found: C, 63.30; H, 6.03; N, 9.58.

7-Norbornadienyl Thio- (11) and Isothiocyanate (12).—To a solution of 10.6 g (0.084 mol) of 7-norbornadienyl chloride[8] (4 Cl) in 500 ml of dry acetone was added 86.0 g (0.88 mol) of potassium thiocyanate. The mixture was stirred at room temperature for 17 hr, then poured into ice water, and extracted with pentane. The combined extracts were washed with water and dried over magnesium sulfate; the pentane was evaporated. Distillation of the residue yielded 8.3 g (67%) of a mixture of **11** and **12**, bp 58–60° (0.08 mm). Gc analysis indicated a 95:5 ratio of **11** to **12**.

7-Norbornadienyl Thiocyanate (11).—Since the isolation of thiocyanate **11** from the mixture by column chromatography was not successful due to decomposition of both **11** and **12** on silica gel, the following procedure was used.

To a solution of 0.15 g (2.1 mmol) of *tert*-butylamine in 5 ml of purified dioxane was added 2.0 g (0.013 mol) of mixture. The solution was stirred at room temperature for 4 hr and work-up was similar to that employed for the isolation of *anti*-7-norbornenyl thiocyanate (**7**). The crude product was distilled affording 1.35 g of **11**: bp 53.5–55.0° (0.07 mm); ir (film) 2950, 2140, 1300, 1240, and 800 cm^{-1}; nmr ($CDCl_3$) τ 6.1 (sextet), 3.25 (triplet), 3.15 (triplet).

Anal. Calcd for C_8H_7NS: C, 64.39; H, 4.73; N, 9.39. Found: C, 64.55; H, 4.67; N, 9.24.

The crude 1-(7-norbornadienyl)-3-*tert*-butylthiourea, obtained as a by-product above, was recrystallized from ether–pentane after use of decolorizing carbon giving white crystals: mp 179.5–180.0°; ir (Nujol mull) 3200, 2900, 1520, 1450, 1190, and 730 cm^{-1}.

Anal. Calcd for $C_{12}H_{18}N_2S$: C, 64.82; H, 8.12; N, 12.60. Found: C, 64.62; H, 8.01; N, 12.40.

7-Norbornadienyl Isothiocyanate (12).—A solution of 0.688 g (4.6 mmol) of **11** in 60 ml of acetonitrile was sealed into a Pyrex tube and heated at 80° for 7.5 hr. The tube was opened and the contents were poured into 200 ml of water. The product was extracted with pentane and the combined extracts were washed with water and dried over magnesium sulfate. The pentane was evaporated and the distillation of the crude product gave 0.375 g (55%) of **12**: bp 42–44° (0.08 mm); ir (film) 2926, 2200, 2100, 1330, 1310, 1230, 1190, 1110, and 815 cm^{-1}; nmr ($CDCl_3$) τ 6.25 (sextet), 3.25 (triplet).

Anal. Calcd for C_8H_7NS: C, 64.82; H, 8.12; N, 12.60. Found: C, 64.91; H, 8.11; N, 12.53.

Product Studies.—Approximately 0.05 *M* solutions of **7** or **11** in purified sulfolane, acetonitrile, dimethylformamide, or tetramethylurea were sealed in glass ampoules under a nitrogen atmosphere and heated at constant temperatures ranging from 40 to 130° for various times. After quenching by cooling, the material was reisolated by subjecting these solutions to water and extraction with pentane, followed by drying and concentration of the extracts. Material recovery was always in excess of 95% (crude); thus the material was analyzed directly by nmr infrared, tlc (silica gel support with cyclohexane as liquid phase), and gc (see kinetic studies section for conditions and retention times). Both starting material, thiocyanate, and product, isothiocyanate, were always homogeneous to those methods of analysis.

Isomerizations in the Presence of Salts.—Product studies were carried out as previously described except the 0.05 *M* solutions of **7**, **8**, or **11** were also 0.1–0.5 *M* in potassium thiocyanate, lithium perchlorate, or tetraethylammonium azide. Material recovery was the same as before with the exception of the azide solutions of **7** and **11** where a pentane-insoluble, ether-soluble brown tar was also isolated. The pentane extracts in these cases (10–15% of the original mixture) consisted only of the corresponding alkyl azide by gc analysis.

Kinetic Studies.—The following methods were employed for analysis.

Method A.—Solutions approximately 0.04 *M* in pure **7** were prepared using sulfolane as a solvent. Aliquots (5 ml) were sealed in glass tubes and heated at the appropriate temperature in a constant temperature bath. The tubes were removed at various time intervals and quenched by immersion in cold water, and the contents were poured into 20.0 ml of 0.019 *N* *n*-butylamine in dioxane. These mixtures were allowed to stand overnight protected from moisture and titrated with 0.01 *N* hydrochloric acid to the methyl red end point.

Method B.—Solutions about 0.04 *M* in pure **7** were made using dimethylformamide, tetramethylurea, acetonitrile, and sulfolane. The solutions were placed in 50-ml flasks fitted with septum caps and heated at 110.0 ± 0.5, 80 ± 0.1, or 130.0 ± 0.1°. Aliquots (3 ml) were drawn from the flasks by a syringe at various time intervals and quenched with cold water. The aliquots were poured into 30 ml of water and extracted with pentane, and the combined extracts were washed with water and dried over magnesium sulfate. Evaporation of the pentane gave residues which were analyzed by gc using a 2 ft × 0.25 in. LAC-728 column (temperature 115.0°, carrier flow 85 ml/min; R_t (min) **8**, 4.4; **7**, 10.1).

Method C.—Aliquots (3 ml) of acetonitrile solutions approximately 0.04 *M* in **11** were sealed in glass tubes and heated at 80.0 ± 0.5 and 59.0 ± 0.5°. Tubes were removed at various time intervals, quenched by immersion in cold water, and stored at −20° until used. The work-up was similar to method B. Gc analyses were carried out by using a 2 ft × 0.25 in. QF-1 column (temperature 95°, carrier flow 260 ml/min; R_t (min) **12**, 3.6; **11**, 9.6).

Registry No.—**7**, 28273-26-9; **8**, 28273-27-0; **11**, 28273-28-1; **12**, 28273-29-2; 1-(*anti*-7-norbornenyl)-3-*n*-butylthiourea, 28273-30-5; 1-(7-norbornadienyl)-3-*tert*-butylthiourea, 28312-60-9.

Acknowledgment.—We are grateful to the Petroleum Research Fund administered by the American Chemical Society (Grant No. 2925-Al) for generous support of this research.