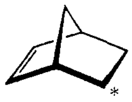
Allylcarbinyl–Cyclopropylcarbinyl Norbornenyl–Nortricyclyl Anion Rearrangement. Evidence for a Symmetrical Intermediate[1a]

J. K. Stille* and K. N. Sannes[1b]

Contribution from the Department of Chemistry, University of Iowa, Iowa City, Iowa 52240. *Received June 1, 1972*

Abstract: The synthesis of *exo*-6-deuterio-*exo*-5-norbornenylhydrazine (**12**), *exo*-5-norbornenylhydrazine (**11**), and 3-nortricyclylhydrazine (**13**) (hydrogen oxalates) are described. The basic oxidative cleavage reactions of either **11** or **13** in water or *tert*-butyl alcohol-*O-d* afforded a 57:43 mixture of nortricyclene to norbornene. The reaction of **12** in water provided a norbornene fraction in which the deuterium label was distributed equally between the anti-7 and exo-5 positions. A mechanism that explains these results involves either a symmetrical nonclassical anion intermediate (**25**) or a classical 3-nortricyclic anion (**23**) that opens to afford scrambling between the 2 and 7 positions of the norbornenyl anions (**22** and **24**).

Mesomerization occurs between structures **1** and **2** in reactions where cationic,[2] radical,[3] and anionic[4] intermediates have been postulated. Reactions with cationic intermediates predominantly form products that have the tricyclic skeleton,[2] while the tendency for radical and anionic reactions is toward a more even distribution of tricyclic and norbornenyl products.[3,4] The radical intermediates corresponding to **1** and **2** have each been independently generated, and the product was shown to be comprised of identical ratios of norbornene and nortricyclene.[3]



1

2

3

The reaction of *exo*-2-chloronorbornene and 3-chloronortricyclene with sodium resulted in a mixture of C-7 hydrocarbons in which the ratio of norbornene to nortricyclene depended, among other factors, on the starting alkyl chloride.[4]

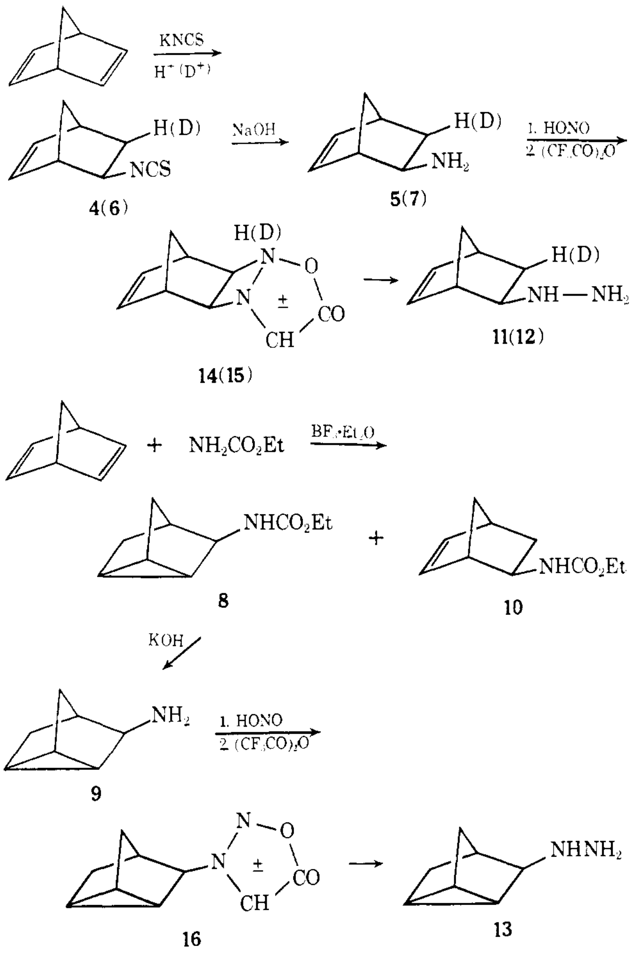
The nature of the intermediate that allows interconversion between cations **1** and **2** also has been studied.[5–7] The evidence suggests the existence of a symmetrical nonclassical intermediate such as **3** or a rapid equilibration between classical cations corresponding to **1** and **2**.

This paper concerns the independent generation of anions corresponding to **1** and **2** to observe the amount of mesomerization that occurs before their capture of hydrogen. Also a more detailed examination of the intermediate for this mesomerization was carried out with an appropriately deuterium labeled precursor.

Results

Norbornadiene was allowed to react with potassium thiocyanate (Scheme I) under acidic conditions[8] to yield *exo*-5-norbornenyl 2-isothiocyanate (**4**). By using sodium hydroxide instead of the potassium hydroxide reported[8] and by carefully selecting the reaction time and temperature, the yield from the hydrolysis of **4** to

Scheme I



---

[1] (a) Abstracted in part from the Ph.D. thesis of K. N. Sannes, University of Iowa, Jan 1972; (b) NASA Trainee, 1969–1971.

[2] M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967), and references therein.

[3] C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

[4] P. Freeman, D. George, and V. Rao, *ibid.*, **29**, 1682 (1964).

[5] S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *J. Amer. Chem. Soc.*, **88**, 3087 (1966).

[6] J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **77**, 3034 (1955).

[7] C. C. Lee and B.-S. Hahn, *ibid.*, **92**, 2583 (1970).

[8] W. R. Diveley, G. A. Buntin, and A. D. Lohr, *J. Org. Chem.*, **34**, 616 (1969).

exo-5-aminonorbornene (**5**) was approximately doubled. After distillation, **5** was sufficiently pure to use in the next step. The same sequence of reactions, except for the use of a deuterated solvent system in the first reaction, afforded *exo*-6-deuterio-*exo*-5-norbornenyl isothiocyanate (**6**) and *exo*-6-deuterio-*exo*-5-aminonorbornene (**7**) as expected.

In the presence of boron trifluoride, norbornadiene and ethyl carbamate react to form 3-*N*-carbethoxyaminonortricyclene (**8**).[9] Distillation afforded a white solid with the same melting point as that reported;[9] however, this material contained an olefin (**10**) which was removed by extraction with silver nitrate. Hydrolysis of **8** and distillation furnished 3-aminonortricyclene (**9**) which was used without further purification.

Amines **5**, **7**, and **9** were converted to *exo*-5-norbornenylhydrazine (**11**), *exo*-6-deuterio-*exo*-5-norbornenylhydrazine (**12**), and 3-nortricyclylhydrazine (**13**), respectively (Scheme I), by the method outlined in the previous paper.[10]

Double resonance experiments on 3-(*exo*-5-norbornenyl)sydnone (**14**) provided additional proof of the exo isomer of that compound. Integration of the appropriate regions of the nmr spectrum of 3-(*exo*-6-deuterio-*exo*-5-norbornenyl)sydnone (**15**) indicated 99% d_1 content at the exo-6 site.

When either **11** (hydrogen oxalate) or **13** (hydrogen oxalate) was allowed to react under the standard basic oxidative conditions (Experimental Section) in either an aqueous or alcoholic solvent, norbornene and nortricyclene in a 43 :57 ratio were the only volatile products that were detected by glpc analysis (Table I). These products were identified by isolating each component (preparative glpc) and comparing the nmr spectra and glpc retention times of each component with authentic samples of norbornene and nortricyclene.

Table I. Base-Catalyzed Oxidative Cleavage Reactions of **11**, **12**, and **13** (Hydrogen Oxalate)

Alkyl-hydrazine[a]	Solvent	Norbornene: nortricyclene ratio[b]
11 or 13	H_2O	43:57
11 or 13	*t*-BuOH[c]	43:57
12	H_2O	45:55[d]

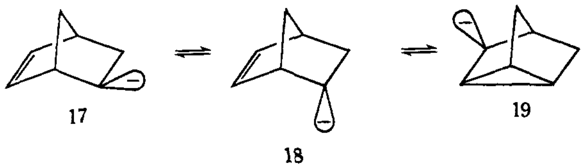
[a] 0.08 *M* in alkylhydrazine, 0.3 *M* in base, 0.08 *M* in potassium periodate. [b] ±2%. [c] Contained 10 mol % H_2O. [d] 50% *exo*-, 50% *anti*-7-deuterionorbornene ±3%.

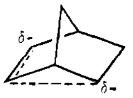
When *exo*-6-deuterio-*exo*-5-hydrazinonorbornene was allowed to react under the standard basic oxidative cleavage conditions in aqueous media, the only products observed were norbornene and nortricyclene in the same 43 :57 ratio. The deuterionorbornene was isolated by preparative glpc. Integration of the appropriate areas of its nmr spectrum showed 50% of the deuterium label now resided at the exo-2 position and the other 50% at the anti-7 position.

Discussion

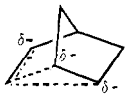
It is evident from the identical 43 :57 norbornene : nortricyclene product ratio (Table I) that, in this homoallylic system, the anions reach an equilibrium before being captured by a proton from the solvent. This equilibrium mixture does not vary with solvent as might be anticipated from previous studies[11,12] in which widely different stereochemistry is realized with the two solvents used.

If equilibrating classical anions are involved, the rates of inversion between anions **17–18** and **19** are rapid compared to their rates of proton capture by solvent. Nonclassical ions **20** and **21** are also intermediates consistent with the fact that an equilibrium exists between the norbornenyl and nortricyclyl skeletons.





20



21

The presence of **19** or **21** makes positions 5 and 7 of the parent norbornene molecule identical; however, intermediate **20** is not symmetrical. The results of the aqueous basic oxidative decomposition of the deuterium labeled hydrazine (**12**) provided a means by which the intervention of a symmetrical (**19**, **21**) or an unsymmetrical intermediate (**20**) could be detected. Intermediates **23** and **25** (Scheme II) afford norbornene with the label evenly distributed between the exo-5 and anti-7 positions. The relative amounts of *exo*-5-deuterionorbornene (**27**) and *anti*-7-deuterionorbornene (**28**) obtained by integration of the appropriate nmr signals[10] show a complete scrambling of deuterium. Therefore unsymmetrical intermediate **26** cannot control crossover between the two valence bond tautomers involved.

Either equilibrating classical anions **22**, **23**, and **24** or the nonclassical intermediate **25** explains the complete equilibration and label scrambling observed.

Experimental Section

Routine nmr analyses were performed on a Varian A-60 and the deuterium analysis on a Varian HA-100 nmr spectrometer internally locked on chloroform at a 250-Hz sweep width. Glpc analyses and isolation of products were performed on Varian 202 B and 1525 C gas chromatographs. Mass spectra were obtained on a CEC 20-103c and on a Hitachi RMU-6 instrument.

***exo*-5-Norbornenyl isothiocyanate (4)** was prepared as previously described[8] in 77% yield from norbornadiene.

***exo*-5-Aminonorbornene (5).** To a solution of 203 g (1.34 mol) of *exo*-5-norbornenyl isothiocyanate in 1725 ml of glycol stirred at about 100° was added 160 g of sodium hydroxide over a period of 10 min. The temperature was 165° after the addition of sodium hydroxide and was maintained there until glpc analysis showed a maximum concentration of **5** present (about 3 hr).

The reaction mixture was cooled and added to 3.4 l. of water which was saturated with potassium carbonate and extracted with benzene (1700-, 500-, and 500-ml portions). The benzene layer was extracted with 320 ml of 10% hydrochloric acid, made basic with 25% sodium hydroxide, saturated with potassium

---

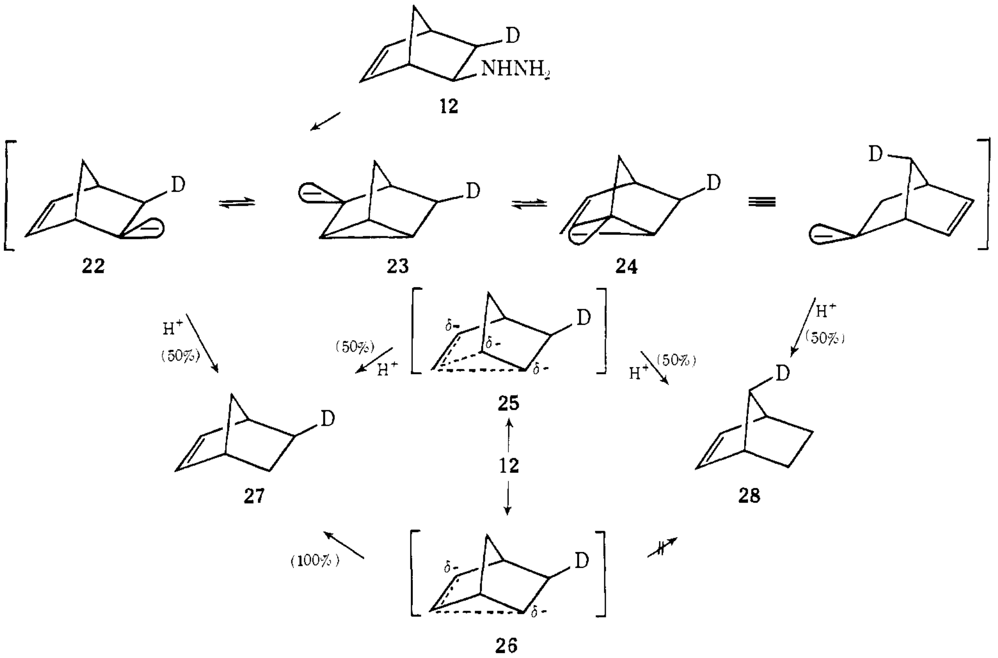
(9) G. Müller and R. Merten, *Chem. Ber.*, **98**, 1097 (1965).

(10) J. K. Stille and K. N. Sannes, *J. Amer. Chem. Soc.*, **94**, 8489 (1972).

(11) (a) D. J. Cram and J. S. Bradshaw, *J. Amer. Chem. Soc.*, **85**, 1108 (1963); (b) D. J. Cram, J. S. Bradshaw, W. Lwowski, and G. R. Knox, *ibid.*, **84**, 2832 (1962).

(12) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

Scheme II



carbonate, extracted with three 300-ml portions of ether, and dried with potassium carbonate. The mixture was filtered, concentrated with a rotary evaporator, and distilled at 70° (40–41 mm) to yield 84 g (57%) of **5**.

3-*N*-Carbethoxyaminonortricyclene (8). The reaction of norbornadiene and ethyl carbamate afforded **8** in 50% yield, mp 64° (lit.[9] 64°); however, glpc analysis at 150° showed the presence of an impurity (~10%) with a shorter retention time, and the nmr spectrum indicated the presence of vinyl protons.

A solution of 100 g of crude **8** in 200 ml of ether and 300 ml of pentane was thoroughly extracted with 100 g of silver nitrate in 100 ml of water. Analysis of the ether–pentane solution by glpc showed removal of the impurity. Removal of the solvent and recrystallization from methanol–water and then cyclopentane afforded a white solid, mp 68–69°. The nmr spectrum was now free of protons in the olefinic region. Hydrolysis of the olefin impurity *exo*-5-carbethoxyaminonorbornene (**10**), which was recovered from the silver nitrate solution, yielded *exo*-5-aminonorbornene, identified by comparison with the nmr spectrum of an authentic sample.

3-Aminonortricyclene[9] (9). The purified carbamate, **8**, was hydrolyzed with the same procedure as that used for the preparation of **5** and distillation at 73–74° (40–41 mm) afforded a 78% yield of **9**.

***exo*-6-Deuterio-*exo*-5-norbornenyl isothiocyanate (6)** was prepared in the same manner as compound **4** with the substitution of D_2SO_4 and D_2O for H_2SO_4 and H_2O.

***exo*-6-Deuterio-*exo*-5-aminonorbornene (7)** was prepared by the same procedure used for the undeuterated amine **5**.

Conversion of Amines 5, 7, and 9 to Their Respective Sydnones 14, 15, and 16. Conversions of the amines to the sydnones was carried out as described in the previous paper.[10]

3-(*exo*-5-Norbornenyl)sydnone (14) has mp 72.5–75.3°; nmr ($CDCl_3$) δ 6.45 (s, 1, sydnone ring), 6.13 and 6.37 (m, 2, =CH), 4.32 (q, 1, C-5); mass spectrum (70 eV) *m/e* 178 for molecular ion (direct inlet). *Anal.* Calcd for $C_9H_{10}N_2O_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.76; H, 5.99; N, 15.53

3-(3-Nortricyclyl)sydnone (16) has mp 83–85°; nmr ($CDCl_3$) δ 6.46 (s, 1, sydnone ring), 4.43 (1, C-3); mass spectrum (70 eV) *m/e* 178 for molecular ion (direct inlet). *Anal.* Calcd for $C_9H_{10}N_2O_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.85; H, 5.28; N, 15.76.

Hydrolysis of Sydnones 14, 15, and 16 to Hydrazine Oxalates 11, 12, and 13, Respectively. Hydrolysis of the sydnones to the hydrazines was carried out by the procedures described in the previous paper.[10]

***exo*-5-Norbornenylhydrazine Oxalate (11).** *Anal.* Calcd for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 49.92; H, 6.52; N, 12.53.

3-Nortricyclylhydrazine Oxalate (13). *Anal.* Calcd for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.00; H, 6.34; N, 12.53.

Basic Oxidative Cleavage Reactions. In aqueous media, the same conditions as those described in previous work[10] were followed except that water was used instead of deuterium oxide.

In *tert*-butyl alcohol, the same conditions as outlined in the previous paper[10] were employed with the exception that *tert*-butyl alcohol was substituted for *tert*-butyl alcohol-*O-d*.

Determinations of the Ratio of 27 to 28. Regions A and B[10] were integrated and the ratios of label content at positions exo-5 and anti-7 were calculated directly.