Anal. Calcd for $C_7H_{14}N_2$: C, 66.10; H, 11.00. Found: C, 66.19; H, 11.00.

1-(*endo*-Norbornyl)-2-*p*-toluenesulfonhydrazide (4). To a cooled solution of 7.0 g (0.056 mol) of *endo*-norbornylhydrazine and 5.6 g (0.056 mol) of triethylamine in 100 ml of dry ether was added a solution of 0.6 g (0.056 mol) of *p*-toluenesulfonyl chloride in 50 ml of dry ether. After allowing the solution to cool for 24 hr, the white precipitate of triethylamine hydrochloride was removed by filtration, and the filtrate was concentrated on a rotary evaporator until crystals began to form. Cooling and filtration yielded 1.5 g (0.0055 mol, 9.8%) of white crystals: mp 83–85; ir (mull) 3400–3100 cm^{-1} (NH), 1600 cm^{-1} (C=N); nmr ($CDCl_3$) δ 1.25 (m, 8, C-3,5,6,7 H), 2.15 (m, 2, C-1,4 H), 2.42 (s, 3, $ArCH_3$), 3.17 (m, 1, C-2 H (exo)), 4.90 (s (very broad), 2, NH) 7.55 (q, 4, Ar H).

Anal. Calcd for $C_{14}H_{20}N_2O_2S$: C, 60.00; H, 7.14. Found: C, 60.11; H, 7.03.

***exo*-Norbornane-d_1 (5).** Diborane, generated[26] by the addition of a solution of 10.6 g (0.075 mol) of freshly distilled boron trifluoride etherate in 25 ml of dry (lithium aluminum hydride) diglyme to 2.1 g (0.055 mol) of sodium borohydride in 25 ml of diglyme, was passed into a solution of 28.8 g (0.30 mol) of norbornene in 75 ml of diglyme held at 5°. The diborane generator was disconnected and 22.2 g (0.30 mol) of propionic acid-*O*-*d* was added to the norbornene solution. A distillation apparatus was connected and the distillate was collected to a temperature of 110° in a Dry Ice–acetone cooled trap. The solid material was dissolved in ether and the solution was washed three times with 50-ml portions of saturated silver nitrate solution. The volume of the solution was reduced to 10 ml and further purification was accomplished by preparative gas chromatography. Mass spectral analysis revealed the deuterium (d_1) content to be 90.42%.

***endo*-Norbornane-d_1 (6).** This compound was prepared as reported.[27] Purification was accomplished by preparative gas chromatography. Mass spectral analysis revealed the deuterium (d_1) content to be 95.78%.

Procedures for the Basic Oxidative Cleavage of 1 and 2.[16,28] Deuterium Oxide Solvent. A solution of 1.80 g (0.008 mol) of potassium periodate and 0.69 g (0.03 g-atom) of sodium in 50 ml of deuterium oxide was placed in a pressure bottle under nitrogen, and the norbornylhydrazine, 1.00 g (0.008 mol), was placed in a vial and suspended in the pressure bottle under nitrogen. After the bottle had been placed in a constant-temperature bath and maintained at 67 ± 1° for 10 min, the hydrazine was dropped into the solution. Norbornane immediately began to sublime on the walls of the bottle. The solution was maintained at 67 ± 1° for 4 hr, cooled, and then extracted with two 10-ml portions of pentane. The pentane extracts were dried with magnesium sulfate and concentrated by distillation. Samples for infrared analysis and mass spectral analysis were obtained by preparative gas chromatography.

***tert*-Butyl Alcohol-*O*-*d* Solvent.** A solution of 1.80 g (0.008 mol) of potassium periodate and 3.62 g (0.032 mol) of potassium *tert*-butoxide in 50 ml of *tert*-butyl alcohol-*O*-*d* (and in one case nonadeuterio-*tert*-butyl alcohol-*O*-*h*) was placed in a pressure bottle under nitrogen, and the norbornylhydrazine, 1.00 g (0.008 mol), was placed in a vial and suspended in the pressure bottle under nitrogen. After the bottle had been placed in a constant-temperature bath and maintained at 67 ± 1° for 10 min, the hydrazine was dropped into the solution. The solution was maintained at 67 ± 1° for 40 hr and cooled, 30 ml of pentane was added, and the solution was filtered. The filtrate was mixed with 150 ml of water, and the pentane layer was removed, dried with magnesium sulfate, and concentrated by distillation. Samples for infrared analysis and mass spectral analysis were obtained by preparative gas chromatography.

Procedure for the Basic Cleavage of 3 and 4.[16] A solution of 0.25 g (0.011 g-atom) of sodium in 25 ml of deuterium oxide was placed in a pressure bottle under nitrogen, and the hydrazine tosylate, 1.00 g (0.0036 mol), was placed in a vial and suspended in the pressure bottle under nitrogen. After the bottle had been placed in a constant-temperature bath and maintained at 67 ± 1° for 10 min, the hydrazine tosylate was dropped into the solution. Norbornane was observed subliming on the walls of the bottle. The solution was maintained at 67 ± 1° for 4 hr, cooled, and extracted with two 10-ml portions of pentane. The pentane extracts were dried with magnesium sulfate and concentrated by distillation Samples for infrared analysis and mass spectral analysis were obtained by preparative gas chromatography. The procedure for the *exo*-hydrazine tosylate is identical with that outlined above.

Infrared Analysis of Epimeric Compositions of *exo*- and *endo*-Norbornane-d_1. These analyses were carried out using characteristic bands assigned in the 1000–700-cm^{-1} infrared region.[27] The 894-cm^{-1} band for *exo*-norbornane-d_1 and the 836-cm^{-1} band for *endo*-norbornane-d_1 were chosen as the analytical frequencies because of their intensity and clarity. Mixtures of "known" epimeric composition were prepared from authentic samples of *exo*- and *endo*-norbornane-d_1 and found to obey Beer's law. Relationships between concentration and absorbance were determined by the method of least squares and used to determine the composition of the unknown product mixtures. Good agreement between total deuterium (d_1) content (*exo*-d_1 + *endo*-d_1) as determined by this method and low ionization potential mass spectral determinations was obtained.

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(27) A. Nickon and J. Hammons, *J. Amer. Chem. Soc.*, **86**, 3323 (1964).
(28) Identical results were obtained when the hydrazine oxalate was used directly.

7-Norbornenyl Anions. Evidence for a Bishomoantiaromatic System[1a]

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

Abstract: The synthesis of *anti*- (**13**) and *syn*-7-norbornenylhydrazine (**14**) is described. Production of the 7 anion by basic oxidative cleavage of **13** and **14** in deuterium oxide and **14** in *tert*-butyl alcohol-*O*-*d* afforded *anti*- (**7**) and *syn*-7-deuterionorbornene (**8**), in approximately a 94:6 ratio, as the sole products of deuteron capture. This preference for anti capture can be explained in terms of an equilibrated mixture of *anti*- (**24**) and *syn*-7-norbornenyl anion (**25**) intermediates that contain predominantly **24**. The bishomocyclopropenyl anion **25** is less stable than **24** as a result of the antiaromatic character of the former.

Carbocyclic systems (**1**) in which the developing reaction site is symmetrically attached to an olefin moiety by means of two methine (or methylene) groups are of interest because of the possible existence of the bishomocyclopropenyl[2–4] intermediate **2**. *anti*-

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

(2) R. Breslow, R. Pagni, and W. Washburn, *Tetrahedron Lett.*, 547 (1970).
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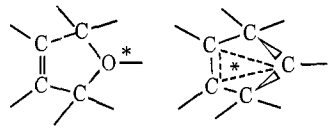
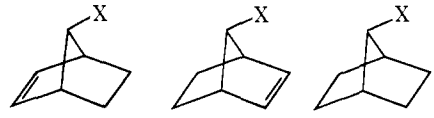
7-Tosyloxynorbornene (**3**), for example, solvolyzes 10^{11} times faster than the saturated 7-tosylnorbornane (**4**)[5] and affords exclusively anti solvolysis products.[6,7]



1 2



3, X = OTs
5, X = Br
7, X = D
9, X = CN
11, X = CO_2Et

6, X = Br
8, X = D
12, X = CO_2Et

4, X = OTs
10, X = CN

The same stereospecificity is observed in the aqueous solvolysis of **3** in the presence of sodium borodeuteride, where the cation is captured by deuteride.[8] The enhanced rates and the stereospecificity observed suggest the formation of intermediate **2** in these and other reactions that involve cationic intermediates.[3,4]

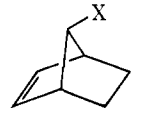
The reduction of *anti*- (**5**) and *syn*-7-bromonorbornene (**6**) with tri-*n*-butyltin deuteride, a type of reaction postulated to proceed *via* a free radical intermediate, also provided norbornene deuterated at the 7 position.[9] Although preliminary results indicated that *anti*-7-deuterionorbornene (**7**) was the only product present, evidence now shows[10,11] that *syn*-7-deuterionorbornene (**8**) is formed in appreciable amounts (~30%). The lower stereospecificity in this case discredits somewhat the original argument favoring a nonclassical 7-norbornenyl radical intermediate.[9]

By analogy with the cyclopropenyl anion[12] it could be expected that an anion generated at the 7 position of norbornene with the appropriate syn geometry would inherit the increased energy that attends a system with antiaromatic character. A comparison of the rates of proton abstraction from *anti*-7-cyanonorbornene (**9**) and 7-cyanonorbornane (**10**) was not very conclusive; however, the possibility of some kinetic retardation due to antiaromaticity was demonstrated. The 2:1 anti:syn product ratios, which were observed for the carbonation and oxidation reactions of the Grignard reagent formed by treating **6** with magnesium,[13] were attributed to a repulsion of the negative charge on the anion by the π electrons of the double bond.[13a] This preference was not attributed to steric effects, because the equilibrum mixture of *anti*- (**11**) and *syn*-7-carboethoxynorbornene (**12**) contains 55% of the latter.[13b] However, the intermediate in this base-catalyzed isomerization should also be anionic and could be a dominant factor in determining this equilibrium ratio.

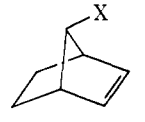
SCF–MO calculations predict[14] that the 7-norbornenyl cation has a strong three-center bond which becomes progressively weaker as electrons are added to antibonding orbitals to form the radical and finally the anion; the anion should possess over-all antibonding character. The nature of anionic intermediates generated at the 7 position of norbornene is the principal concern in this work. The products of these reactions with anionic intermediates, especially when viewed in relation to the results of the reactions that proceed by cationic and radical intermediates, should provide information concerning the nature of this anion. To this end, *anti*- (**13**) and *syn*-7-norbornenylhydrazine (**14**) were synthesized and individually subjected to a basic oxidative cleavage reaction that is proposed to proceed by carbanionic intermediates.[15]

Results

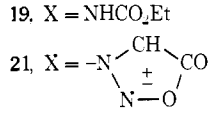
The synthetic pathway that was developed for the preparation of **13** and **14** from *anti*- (**15**) and *syn*-7-aminonorbornene (**16**), respectively, utilized a combination of existing procedures with a number of modifications, some of which proved to be critical. Compound **16** was prepared according to an established procedure,[16] while **15** was prepared by reducing 7-oxyiminonorbornene (**17**) with aluminum hydride. Aluminum hydride had been reported to reduce oximes to amines under mild conditions[17] and in better yields than those obtained with other metal hydrides. The reduction of **17** with aluminum hydride proceeded smoothly; however, a mixture of **15** and 7-aminonorbornane (**18**) in a 7:3 ratio was obtained. After protecting the amine groups by allowing the crude reduction mixture to react with ethyl chlorocarbonate to form *anti*-7-*N*-carbethoxyaminonorbornene (**19**) and 7-*N*-carbethoxyaminonorbornane (**20**), it was possible to purify **19** by selectively complexing it with silver nitrate in an aque-



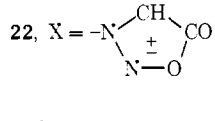
13, X = $NHNH_2 \cdot (CO_2H)_2$
15, X = NH_2
19, X = $NHCO_2Et$



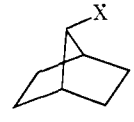
14, X = $NHNH_2 \cdot (CO_2H)_2$
16, X = NH_2



21, X = –N(CH)(CO)N⁺–O⁻



22, X = –N(CH)(CO)N⁺–O⁻



18, X = NH_2
20, X = $NHCO_2Et$

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(14) H. O. Ohorodnyk and D. P. Santry, *J. Amer. Chem. Soc.*, **91**, 4711 (1969).
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(16) H. Tanida, T. Tsuji, and T. Irie, *J. Org. Chem.*, **31**, 3941 (1966).
(17) H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, **90**, 2927 (1968).

Table I. Base-Catalyzed Oxidative Cleavage Reactions of **13** and **14**

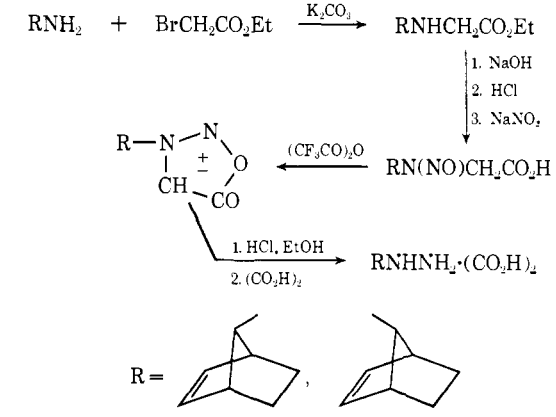
Alkylhydrazine[a]	Solvent	d_1 content: Mass spec, ±0.1%	d_1 content: Nmr, ±6%	d_1 location: Anti, ±5%	d_1 location: Syn, ±5%	Yield, %
13	D_2O	95.9	93	93	7	40
14	D_2O	94.9	95	95	5	49
14	*t*-BuOD[b]	52.1	52	94	6	25

[a] 0.08 *M* in alkylhydrazine, 0.3 *M* in base, 0.08 *M* in potassium periodate. [b] Contained 10 mol % D_2O.

ous solution, in a manner analogous to that used to purify the syn isomer[16] **16**.

The types of products involved in converting amines to hydrazines by the route shown in Scheme I are

Scheme I

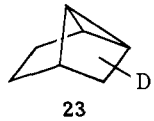


known.[18] To avoid unnecessary loss of material, an intermediate was purified only to the extent required by a subsequent step in the synthesis. The nmr spectra of each of the crude intermediates agreed with those expected. The sydnones, *anti-* (**21**) and *syn*-7-norbornenylsydnone (**22**), were obtained as pure compounds which were hydrolyzed to their respective hydrazines and isolated by precipitation as the oxalate salt. The nmr spectrum of each salt in D_2O showed the olefin protons and other expected characteristics of the desired **13** and **14**.

The method used to determine the ratio of **7** to **8** in the products of basic oxidative cleavage involved a comparison of the appropriate areas in the nmr spectra. To establish the validity of this method of analysis, compounds **7** and **8** were independently synthesized. Compound **8** was synthesized by a sequence analogous to that used previously to synthesize **7**[8] (Scheme II).

Comparison of the nmr spectra of compounds **7** and **8** in benzene-d_6 showed clearly the anticipated anti and syn incorporation of deuterium, respectively. Integration of these two spectra also verified the validity of using this method for the determination of the relative amounts of **7** and **8** in the product mixture.

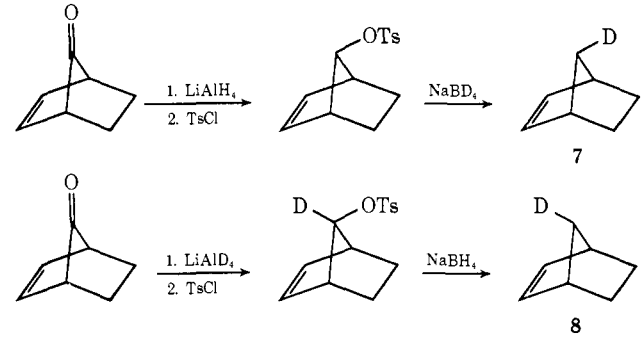
In the course of preparing **7** and **8**, compound **23** was



23

also obtained but could be separated on a nonpolar glpc column. Thus, the ability to differentiate between compounds **7** or **8** and **23**, a possible product in these reactions with 7-norbornenyl anion intermediates, was established.

Scheme II



The results of the base-catalyzed oxidative cleavage reactions of **13** and **14** are given in Table I. The product mixtures were first analyzed by glpc to determine the nature and relative amounts of each component and each component was then isolated by preparative glpc. The total deuterium content of each product was determined by mass and nmr spectroscopy and the locations of this deuterium were determined by nmr at 100 MHz.

A relative downfield shift occurred in the nmr spectrum for the syn-7 proton of norbornene when benzene was the solvent as compared to when carbon tetrachloride (or chloroform) was used as a solvent. This downfield shift serves to reinforce the current assignment[8,19] of this absorption to the syn-7 proton. More important was the resulting increase in separation of the resonances of the syn- and anti-7 protons that occurred when benzene was the solvent, since it facilitated the determination of the anti to syn deuterium ratio in norbornene (see Figure 1).

When **13** and **14** were subjected to standard SEI reaction conditions (see Experimental Section and Table I) the resulting product mixtures were shown by glpc analysis to contain two volatile components. One component had a retention time identical with that of norbornane and was 2.0 to 2.5% of the volatile products. The low yield of this component precluded the isolation of a sufficient amount of material for structure determination. However, it is believed that this component is norbornane which was derived from the similarly small percentage of saturated amine, **18**, present in **15** and **16** from which **13** and **14** were prepared.

The other component, which was 97.5–98% of the volatile reaction products, was norbornene as determined by its glpc retention time and from its nmr spectrum. No tricyclo product, **23**, was detected.

(18) H. V. Daeniker, *Helv. Chim. Acta*, **50**, 2008 (1967); (b) J. Fugger, J. M. Tien, and I. M. Hunsberger, *J. Amer. Chem. Soc.*, 77, 1843 (1955); (c) R. A. Eade and J. C. Earl, *J. Chem. Soc.*, 591 (1946); (d) J. K. Stille, W. A. Feld, and M. E. Freeburger, *J. Amer. Chem. Soc.*, **94**, 8485 (1972).

(19) B. Franzus, W. C. Baird, Jr., N. F. Chamberlain, T. Hines, and E. I. Snyder, *ibid.*, **90**, 3721 (1968).

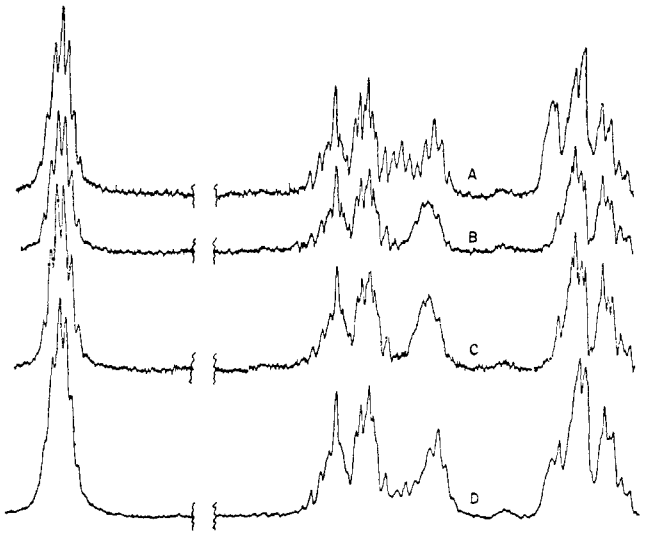
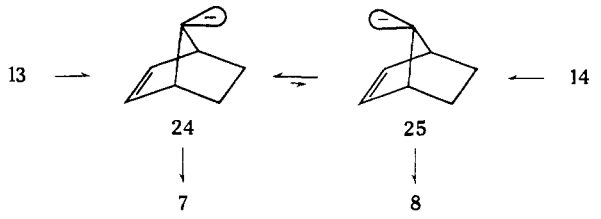


Figure 1. Nmr spectra of norbornene and the deuterated norbornenes resulting from the basic oxidative cleavage reactions of **13** and **14**. The bridgehead region is on the left; the exo-5,6 syn-7 region in the center, and the anti-7 endo-5,6 region on the right. (A) Norbornene; (B) from **13**·hydrogen oxalate in D_2O; (C) from **14**·hydrogen oxalate in D_2O; (D) from **14**·hydrogen oxalate in *t*-BuOD. These spectra were obtained at 100 MHz with a 250-Hz sweep width in 0.4 ml of hexadeuteriobenzene and 0.1 ml of chloroform; the downfield vinyl protons are not shown.

The strong preference for anti deuterium incorporation and the fact that the anti:syn ratio of deuterium did not depend on the solvent or the starting materials (Table I), as might have been expected from previous studies,[15a-c] is consistent with the following. Anions **24** and **25** are formed in a slow, irreversible step from **13** and **14**, respectively, and equilibrate before they are captured by deuterium, to afford the observed 94:6 ratio of **7** to **8**.



The stereospecificity induced by specific solvents in reactions with optically active molecules[15a-c] was not detected and must be small by comparison with other influences in this 7-norbornenyl system.

The implied predominance of **24** over **25** is the result of a destabilizing effect experienced by the latter anion. This syn anion has a significant amount of antiaromatic character because of three-center antibonding interactions which result in a higher energy of **25** as compared to **24**. By contrast, the exclusive formation of antisubstituted norbornenes and also the large amount of tricyclic product (**23**) obtained from 7-norbornenyl cation intermediates have been attributed to the strong three-center bonding.[4,8]

Capture of the proposed 7-norbornenyl radical intermediate[9-11] has resulted in approximately a 70:30 ratio of **7** to **8** and no tricyclic products. The radical intermediate would be expected to possess a propensity for a three-center bonding intermediate between that of the cation and anion;[14] the three-center bond may not be strong enough to induce exclusive anti attack by the incoming group, as is the case for the cation, and neither does it possess the overall antibonding character of the anion, which also gives rise to anti-incorporation of the incoming group.

If the ratio of the rates of capture of anions **24** and **25** was not *one* the ratio of deuterated products would not accurately reflect the ratio of anions **24** and **25** in the equilibrium mixture. However the fact that two solvents with widely differing steric requirements, acidities, and dielectric constants gave the same ratio of products is evidence for a rate of capture ratio of close to one. Also, we could find no compelling evidence in the literature favoring a preference for anti over syn attack on the basis of steric requirements.

Experimental Section[20]

anti- (**7**) **and** *syn*-**7-Deuterionorbornene** (**8**). *anti*-7-Deuterionorbornene was prepared as described.[8] The scheme used for the preparation of **8** was the same as that used to prepare **7** except that lithium aluminum deuteride was substituted for lithium aluminum hydride in the reduction of **17** and sodium borohydride was substituted for sodium borodeuteride in the final solvolysis step.[8]

7-Oxyiminonorbornene (**17**). The same procedure as used in a prior study[16] afforded a product which solidified easily at room temperature before distillation. Crude **17** was sublimed at 70° (1.4 mm) to give an 81% yield of a white solid: mp 82–84°; bp 100° (3 mm); reported,[16] oil, bp 70–73° (3 mm).

Aluminum Hydride Reduction of 17. A mixture of 15.2 g (0.4 mol) of lithium aluminum hydride in 600 ml of tetrahydrofuran was stirred and placed in an ice bath while 19.6 g (0.2 mol) of sulfuric acid was added dropwise under nitrogen.[17] To this mixture stirred at room temperature was added slowly a solution of 24.6 g (0.2 mol) of **17** in 150 ml of tetrahydrofuran. The reaction mixture was hydrolyzed with 100 ml of a 1:1 mixture of tetrahydrofuran and water followed by 20 g of sodium hydroxide in 200 ml of water. The mixture was filtered, the residue was extracted with three 200-ml portions of ether, and the combined extracts were dried with potassium carbonate. Glpc analysis on a 5-ft × 0.25-in. 5% SE-30 on Chromosorb W column at 90° indicated 69% of **15** and 31% of another component (**18**). This solution was used directly in the next step.

Conversion of Amines 15 and 18 to Carbamates 19 and 20. To the dried ether solution from the aluminum hydride reduction of **17** was added 140 ml of dry pyridine, and this solution was stirred and immersed in an ice bath while 21.2 g (0.196 mol) of ethyl chlorocarbonate in 125 ml of ether was added slowly. The reaction was allowed to proceed at room temperature overnight and the mixture was then filtered and concentrated with a rotary evaporator. The residue was dissolved in 500 ml of ether, washed with five 50-ml portions of 10% hydrochloric acid and 60 ml of water, and dried with magnesium sulfate. The solution was filtered and the ethers were removed to afford 25.05 g (0.139 mol, 70% based on **17**) of a mixture of carbamates in the same ratios (69:31 as determined by glpc analysis on a 5-ft × 0.25-in. 5% SE-30 on Chromosorb W column at 145°) as their amine precursors.

Purification of Carbamate 19 (or *syn*-**7-Carbomethoxyaminonorbornene)**[16] **with Silver Nitrate.** The crude carbamates from the previous step were dissolved in 150 ml of pentane and extracted with 100 ml of a saturated solution of silver nitrate in water, and the phases were separated. The aqueous layer was treated with about 600 ml of ammonium hydroxide (30% ammonia), extracted with pentane, dried with magnesium sulfate, filtered, and concentrated to yield 13.0 g (0.072 mol; 75% of original **19** present in the crude mixture) of carbamate **19**.

anti-**7-Aminonorbornene** (**15**). The procedure was the same as that used for the preparation of the syn isomer.[16] Distillation at 72–74° (42 mm) gave a 75% yield of a waxy solid as described.[16]

Conversions of Amines 15 and 16 to Sydnones 21 and 22, Respectively. Reactions of Amines 15 and 16[16] **with Ethyl Bromo-**

(20) Routine nmr analyses were performed on a Varian A-60 and the deuterium analyses on a Varian HA-100 nmr spectrometer internally locked on chloroform at a 250-Hz sweep width. Glpc analysis 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.

acetate to Obtain Ethyl Glycinate Intermediates. To a solution of 1 mol of amine in 600 ml of benzene were added slowly 130 g of potassium carbonate and 65 ml of water with vigorous stirring. This stirred mixture was cooled in an ice bath and a solution of 1 mol of ethyl bromoacetate in 220 ml of benzene was added at a very slow drop rate. The stirred mixture was allowed to come to room temperature during an additional 12 hr of reaction time. A solution of 30 g of potassium carbonate in 60 ml of water was then added, and the reaction mixture was stirred for an additional 12 hr. The reaction mixture was washed with 700 ml of water, dried with magnesium sulfate, filtered, concentrated on a rotary evaporator, and distilled at 68–80° (0.1 mm) in a short-path system to remove most of the disubstituted materials.

Hydrolysis of Glycine Esters and Isolation of Glycine Hydrochloride Salts. A mixture, prepared by adding 1 mol of glycine ester to a solution of 1.1 mol of sodium hydroxide in 190 ml of water, was stirred at about 80° until the mixture became homogeneous (about 20 min). The solution was cooled and acidified with a 2:1 mixture of concentrated hydrochloric acid and water (1.1 mol of HCl). The liquids were removed on a rotary evaporator, and the white solids were used in the nitrosation step without further purification.

Nitrosation of Glycine Hydrochlorides. The solids from the previous reaction (maximum of 1 mol) were dissolved in 660 ml of water. The resulting solution was cooled in an ice bath and stirred while 1.1 mol of sodium nitrite in 200 ml of water was added at a rapid drop rate. The reaction mixture was refrigerated for 4 hr, extracted with ether, and dried with magnesium sulfate. Filtration and removal of the solvent left a yellow solid or semisolid that was used directly in the next step.

Conversion of the Nitroso Derivatives to Sydnones 21 and 22 with Trifluoroacetic Anhydride. To 1 mol of the crude nitroso derivative, dissolved in 1 l. of ether and 0.5 l. of methylene chloride cooled to 0° and stirred was added dropwise a solution of 450 ml of trifluoroacetic anhydride[14] in 450 ml of ether. The solvents and excess trifluoroacetic anhydride were removed; the residue was taken up in 1 l. of chloroform, washed well with 10% aqueous sodium bicarbonate solution, and dried. Filtration and removal of the solvent left a brown residue which crystallized upon refrigeration.

21: mp 92–93°; nmr ($CDCl_3$) δ 6.28 (s, 1, sydnone ring) 6.19 (t, 2, vinyl) 4.08 (m, 1, C_7); 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, 5.29; N, 15.71.

22: mp 80.5–82°; nmr ($CDCl_3$) δ 6.26 (s, 1, sydnone ring), 5.98 (m, 2, vinyl), 4.21 (m, 1, C_7); 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, 60.60; H, 5.89; N, 15.42.

Hydrolysis of 21 and 22 to 13 and 14. A solution of 2.5 g (12.9 mmol) of **21** and **22** in 17 ml of absolute ethanol and 12 ml of concentrated hydrochloric acid was placed in an oil bath maintained at 76° for 1.5 hr. The solution was cooled in ice and treated with a solution of 4.5 g of sodium hydroxide dissolved in 70 ml of water. The resulting mixture, which was still acidic, was extracted with ether to remove unchanged sydnone. An additional 1.55 g of sodium hydroxide, which was dissolved in 17 ml of water, was then added to the aqueous solution. The solution, which was now slightly basic, was saturated with potassium carbonate and extracted with three 12-ml portions of ether. The ether extracts were dried with anhydrous potassium carbonate and filtered. To this solution, stirred at room temperature, was added slowly a solution of anhydrous oxalic acid in absolute ethanol. The oxalate salt precipitate was allowed to stand for at least 6 hr and filtered. The crude hydrogen oxalates of **13** and **14** were recrystallized from methanol–ethanol (1:9) and then from alcohol–ether. The nmr spectrum of each compound in D_2O exhibited the expected relative chemical shifts and the appropriate integrations for each area of resonance.

The yield of crude **13** hydrogen oxalate was 31%, and in addition, 43% of the starting material was recovered. *Anal.* Calcd for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 50.31; H, 6.76; N, 12.19.

The yield of crude **14** hydrogen oxalate was 34%, and 57% of the starting material was recovered. *Anal.* Calcd for $C_9H_{14}N_2O_4$: C, 50.46; H, 6.59; N, 13.08. Found: C, 49.63; H, 7.06; N, 12.62.

Basic Oxidative Cleavage Reactions. In Aqueous Media. To a solution of 0.328 g (0.0084 g-atom) of potassium in 12 ml of D_2O was added 0.345 g (1.5 mmol) of potassium periodate. This solution was purged with ultra-high purity nitrogen, sealed, and placed in an oil bath at 60°. A solution of 0.321 g (1.5 mmol) of hydrazine hydrogen oxalate (**13**- or **14**-hydrogen oxalate) in 6 ml of D_2O was purged with ultrahigh purity nitrogen and added through a septum to the reaction solution. The reaction was allowed to proceed for 2 hr at 60° and then was cooled in ice and extracted with 6 ml of pentane. This pentane extract was concentrated by distillation and purified and isolated with preparative glpc on a 20-ft × 3/8-in. 20% SE-30 on Chromosorb W column at 85°.

In *tert*-Butyl alcohol-*O*-*d*. A mixture, prepared by adding 2.26 g of potassium *tert*-butoxide, 0.805 g (3.5 mmol) of potassium periodate, and 1.3 ml (10 mol %) of D_2O to 42 ml of *tert*-butyl alcohol-*O*-*d*,[21] was purged with ultra-high purity nitrogen gas and placed in an oil bath at 60°. While the mixture was being stirred, 0.75 g (3.5 mmol) of hydrazine hydrogen oxalate was added quickly and the system sealed and allowed to react for 60 hr.

The reaction mixture was cooled, diluted with 5 volumes of water and extracted with 10 ml of pentane. The pentane extract was concentrated by distillation, and the reaction products were analyzed and isolated with glpc on a 20-ft × 3/8-in. 20% SE-30 on Chromosorb W at 85°. The results are presented in Table I.

Determination of the 7 to 8 Ratio by Nmr. The determination of the relative amounts of **7** and **8** in each product mixture involved a comparison of the area due to the exo-5,6 plus syn-7 protons (subsequently referred to as *A*) with that due to the anti-7 plus endo-5,6 protons (subsequently referred to as *B*). After the area due to norbornene[22] had been subtracted from the appropriate regions of the nmr spectrum the quantity, $200(A - S)/S$ (where S = area due to two exo protons = area due to two endo protons = area of the two bridgehead protons[23]) is the per cent of **7** present and the quantity, $200(B - S)/S$, is the per cent of **8** present in the mixture.

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(21) A. T. Young and R. D. Guthrie, *J. Org. Chem.*, **35**, 853 (1970).

(22) This amount of norbornene was determined by mass and nmr spectroscopy.

(23) The two bridgehead protons were used as an internal standard.