2-Norbornyl Anion. Selectivity in Exo/Endo Proton Capture[1]

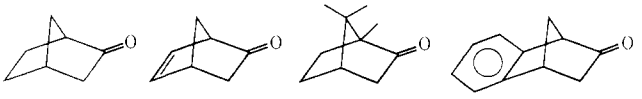
J. K. Stille,* W. A. Feld, and M. E. Freeburger

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

Abstract: The synthesis of *exo*- (**1**) and *endo*-norbornylhydrazine (**2**) as well as their *p*-toluenesulfonhydrazides **3** and **4** are described. The basic oxidative cleavage of **1** and **2** in deuterium oxide and *tert*-butyl alcohol-*O*-*d* and the basic cleavage of **3** and **4** in deuterium oxide were carried out. In all cases, exo-deuterium capture predominates. Either the decomposition of an alkyldiimide intermediate by way of an exo–endo norbornyl anion equilibrium or the decomposition of the alkyldiimide by inversion and retention mechanisms associated with deuterium oxide and *tert*-butyl alcohol-*O*-*d*, respectively, explain the results. Decomposition of **1** and **2** by radical pathways affords results in accord with the modest selectivity of the norbornyl radical for exo capture.

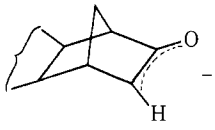
Differences in the facility of attack by reagents at the exo-2 and endo-2 faces of norbornane have been attributed to steric dissimilarities in the respective approach paths.[2,3] This difference in steric hindrance has been cited as the primary factor in providing the enormous exo/endo product ratios in the solvolysis of 2-substituted norbornanes[4,5] and has also been used to account for other observations in reactions involving the 2-norbornyl cation.[6] The magnitude of the exo/endo ratio which is due solely to the steric effect is not necessarily clear in the reaction of norbornyl cations because of the propensity of the cations to suffer rearrangement.

One approach to the question of the relative accessibility of exo *vs.* endo attack at the 2 position in norbornane is obtained from the reaction of the 2-norbornyl anion with electrophiles The rates of exo-3 *vs.* endo-3 proton exchange in. various 2-norbornanones[7–9] range from nearly 2×10^1 to 6×10^2. These values for the exo/endo rate ratios do not as clearly re-



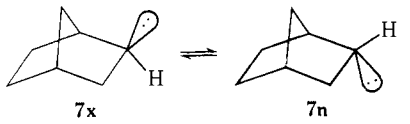
exo	715	9.5	12.4	330
endo	1.0	0.079	0.58	0.59

flect the steric influences as might be anticipated, since proton capture occurs by way of an enolate anion in which the charge is distributed on both the oxygen and



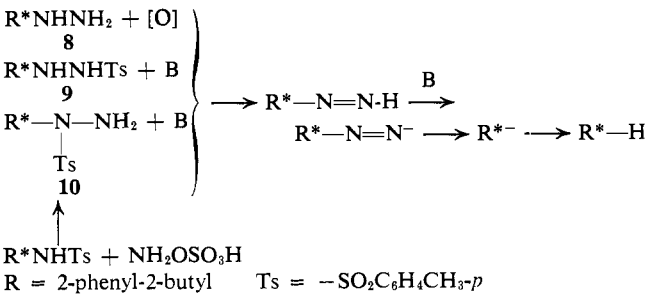
carbon centers. In addition, the steric bulk presented by the carbonyl function is different from that offered by a methylene group.

Capture by 2-norbornyl organometallic compounds has also been studied;[10–15] however, the results in these cases could reflect the intervention of radicals and/or concerted reaction processes. The possibility of radical intermediates, and the partial covalent character of carbon–metal bonds have obscured the observation of the inversion characteristics (**7x** ⇌ **7n**) of the 2-norbornyl anion and associated steric phenemona.



7x **7n**

Thus we have undertaken the generation of a 2-norbornyl anion and the observation of relative ratios of deuteron capture. In the generation of carbanions by the loss of nitrogen (R = 2-phenyl-2-butyl), an alkyldiimide intermediate has been implicated by the fact that optically active **8**, **9**, and **10** afforded the same mixture of products, under the same reaction conditions, within experimental error.[16] When water was used as solvent, inversion was the characteristic stereochemical

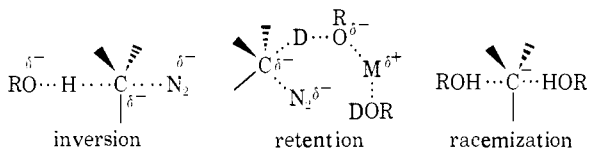


R = 2-phenyl-2-butyl Ts = $-SO_2C_6H_4CH_3$-*p*

pathway as explained by the presence of an unsymmetrically solvated carbanion which was hydrogen bonded at the backside. The use of *tert*-butyl alcohol as solvent was characterized by a retention mechanism since in the low dielectric medium the active form of the

(1) Abstracted in part from the Ph.D. thesis of W. A. Feld, University of Iowa, May 1971; NDEA Fellow, 1967–1970.
(2) H. C. Brown, J. Kawakami, and S. Ikegami, *J. Amer. Chem. Soc.*, **92**, 6914 (1970), and references therein.
(3) H. C. Brown, J. Kawakami, and K.-T. Liu, *ibid.*, **92**, 3816 (1970).
(4) H. C. Brown, *Chem. Soc. Spec. Publ.*, No. 16, 140 (1962).
(5) J. D. Roberts and C. C. Lee, *J. Amer. Chem. Soc.*, 73, 5009 (1951).
(6) H. C. Brown, *Chem. Brit.*, **2**, 202 (1966).
(7) J. Jerkunica, S. Borcic, and D. Sunko, *Tetrahedron Lett.*, 4465 (1965).
(8) P. Barraclough and D. Young, *ibid.*, 2293 (1970).
(9) T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 1448 (1970).
(10) P. Freeman, D. George, and V. Rao, *J. Org. Chem.*, **29**, 1682 (1964).
(11) D. Applequist and G. Chmurny, *J. Amer. Chem. Soc.*, **89**, 875 (1967).
(12) R. Sauers and G. Kwiatkowski, *J. Org. Chem.*, 27, 4049 (1962).
(13) N. Krieghoff and D. Cowan, *J. Amer. Chem. Soc.*, **88**, 1322 (1966).
(14) E. A. Hill, *J. Org. Chem.*, 31, 20 (1966).
(15) F. Jensen and K. Nakamaye, *J. Amer. Chem. Soc.*, **88**, 3437 (1966).
(16) D. J. Cram and J. Bradshaw, *ibid.*, **85**, 1108 (1963).

base is presumed to be associated with solvent and the leaving nitrogen. In the reactions in these solvent systems and others, the conversion of an unsymmetrically solvated carbanion to a symmetrically solvated carbanion afforded racemized product.

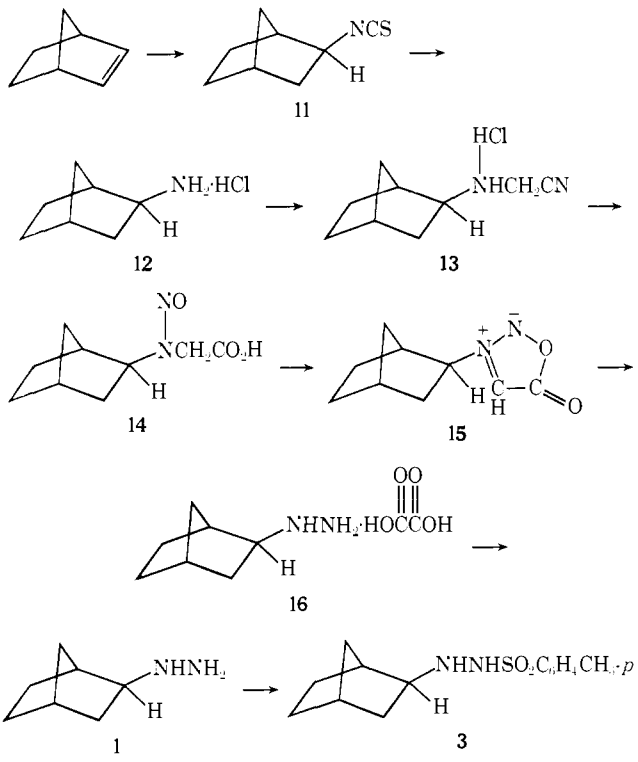


Insufficient base concentration in the basic oxidative cleavage of hydrazine **8**, however, afforded racemized product by a radical mechanism.

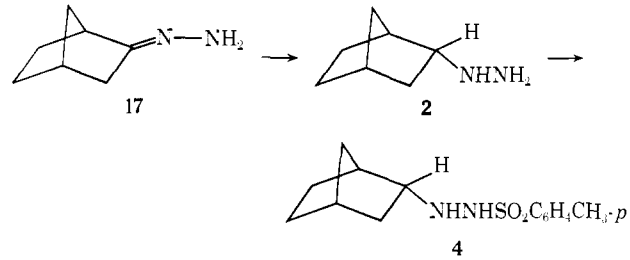
Results and Discussion

The isomeric *exo*- (**1**) and *endo*-norbornylhydrazines (**2**) as well as their *p*-toluenesulfonhydrazides **3** and **4** were synthesized, and basic oxidative cleavage of **1** and **2** and basic cleavage of **3** and **4** were carried out employing deuterium oxide and *tert*-butyl alcohol-*O*-*d* as solvents. The products, *exo*- (**5**) and *endo*-norbornane-d_1 (**6**), were isolated by preparative gas chromatography and analyzed by quantitative infrared spectroscopy.

The addition of isothiocyanic acid to norbornene afforded *exo*-norbornyl isothiocyanate (**11**) which was hydrolyzed with chlorine in acetic acid to yield *exo*-norbornylamine hydrochloride (**12**).[17] The conversion of **12** to *N*-(*exo*-norbornyl)aminoacetonitrile (**13**) was accomplished by treatment of **12** with formaldehyde and potassium cyanide; the product was isolated as the hydrochloride salt. The hydrolysis and nitrosation of **13** afforded *N*-nitroso-*N*-(*exo*-norbornyl)glycine (**14**) which was dehydrated with trifluoroacetic anhydride to give *exo*-norbornylsydnone (**15**). Acid hydrolysis of **15** afforded *exo*-norbornylhydrazine (**1**) which was isolated as the oxalate salt **16** for purification and storage purposes. Treatment of **1** with *p*-toluenesulfonyl chloride and triethylamine in ether afforded 1-(*exo*-norbornyl)-2-*p*-toluenesulfonhydrazide (**3**).



Reduction of norcamphor hydrazone (**17**) with hydrogen employing a platinum oxide catalyst on gelatin gave *endo*-norbornylhydrazine (**2**). Treatment of **2** with *p*-toluenesulfonyl chloride and triethylamine in ether afforded 1-(*endo*-norbornyl)-2-*p*-toluenesulfonhydrazide (**4**).



The stereochemical pathways for the basic oxidative cleavage of **1** and **2** and the basic cleavage of **3** and **4** were expected to parallel those proposed for the 2-phenyl-2-butyl system, *i.e.*, inversion associated with water (D_2O) and retention associated with *tert*-butyl alcohol (*t*-Bu-*O*-*d*) as solvents.

Throughout these studies a strikingly low deuterium content in the reaction products (~60%) was observed when the solvent was *tert*-butyl alcohol-*O*-*d*. Since a large incorporation of hydrogen in our system might imply a nonanionic mechanism, it was necessary to determine the origin of the hydrogen in the products.

When **2** (oxalate salt) was subjected to the basic oxidative cleavage conditions with nonadeuterio *tert*-butyl alcohol-*O*-*h* as the solvent none of the deuterated hydrocarbon was observed in the mass spectrum of the products. Thus, the possibility of proton abstraction from the methyl groups of the solvent was eliminated. The low deuterium contents of the products from the *tert*-butyl alcohol-*O*-*d* reactions can be attributed to a primary deuterium isotope effect.[18]

Based on an 89:11 ratio of OD to OH (calculated for a typical reaction in which the OD is diluted with hydrazine and oxalic acid protons), the 60% deuteration in the products can be accounted for with a deuterium isotope rate ratio of less than 6.

When deuterium oxide was the solvent, an isotope effect was also observed; however, inth is case the deuterium content of the solvent system was much higher (99.8%). In addition, the number of exchangeable deuteriums in D_2O is much higher (and therefore not as easily diluted by hydrogens of the alkyl hydrazine oxalates) than that in *tert*-butyl alcohol-*O*-*d* per given volume of solvent.

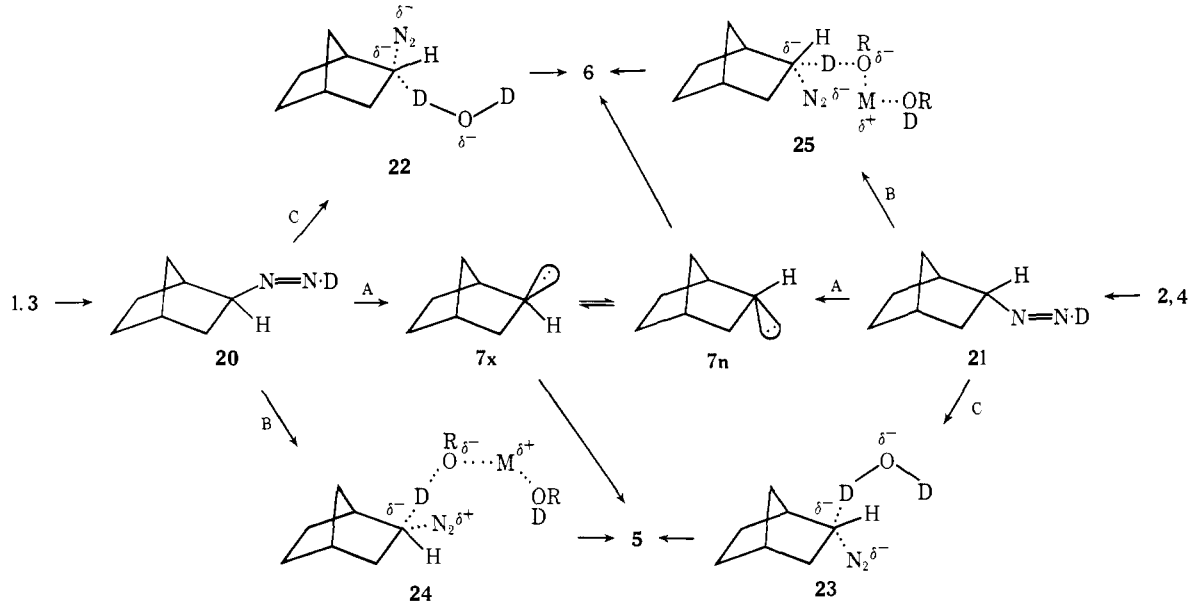
The cleavage of *exo*-norbornylhydrazine (**1**), under conditions which in the case of the 2-phenyl-2-butyl system was shown to proceed with 32% net inversion, afforded a product indicating 74% net retention, 87% *exo*- and 13% *endo*-norbornane-d_1. The cleavage of *endo*-norbornylhydrazine (**2**) under identical conditions afforded a product indicating 100% net inversion, 100% *exo*-norbornane-d_1.

However, cleavage of **1** under retention conditions (*t*-Bu-*O*-*d*), which gave 78% net retention in the case of

(17) W. Diveley, G. Buntin, and A. Lohr, *J. Org. Chem.*, **34**, 616 (1969).

(18) V. Gold and M. A. Kessick, *Proc. Chem. Soc., London*, 295 (1964).

Scheme I



the 2-phenyl-2-butyl system, gave 100% net retention (100% *exo*-norbornane-d_1), and cleavage of **2** under the same conditions gave products indicating 44% net inversion had taken place (72% *exo*- and 28% *endo*-norbornane-d_1; see Table I).

Table I. Cleavages of **1**, **2**, **3**, and **4**

Hydrazine	Reaction conditions[a] at 67°: Solvent base	Time, hr	% exo d_1[b]	% endo d_1[b]
1	D_2O, NaOD	4	87	13
1	D_2O, NaOD	4	86	14
2	D_2O, NaOD	4	100	0
2	D_2O, NaOD	4	100	0
1	*t*-BuOD, *t*-BuOK	40	100	0
1	*t*-BuOD, *t*-BuOK	40	100	0
2	*t*-BuOD, *t*-BuOK	40	72	28
2	*t*-BuOD, *t*-BuOK	40	60	40
1	D_2O, none	4	83	17
2	D_2O, none	4	89	11
3	D_2O, NaOD[c]	4	100	0
4	D_2O, NaOD[c]	4	100	0

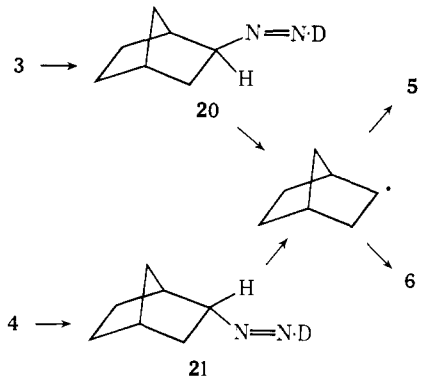
[a] KIO_4 was the oxidizing agent. [b] % exo $d_1 \pm 3$%, % endo $d_1 \pm 3$%. [c] No oxidizing agent.

When deuterium oxide is used as solvent, oxidation of *exo*-norbornylhydrazine (**1**) to alkyldiimide **20** followed by base-catalyzed decomposition of the diimide by way of the asymmetrically solvated carbanion **22** (Scheme I, path C) would yield *endo*-norbornane-d_1 (**6**). Alternately, loss of nitrogen from diimide **20** would allow entry into the **7x**–**7n** equilibrium (path A). Capture of the members of the equilibrium would yield a mixture of products which could represent the position of the exo–endo anion equilibrium. Similar pathways and arguments apply to the cleavage of *endo*-norbornylhydrazine (**2**). Our data are consistent with the intervention of both path A and path C since the cleavage of **1** and **2** proceeding exclusively by path A should yield the same mixture of **5** and **6**. Implication of path C, in the cleavage of **1** at least, hinges on the isolation of 13% *endo*-norbornane-d_1. Further, *endo*-norbornane-d_1 (**6**) must be nearly exclusively formed *via* **22** since conditions promoting racemization in the 2-phenyl-2-butyl system lead to exclusive exo capture in the 2-norbornyl system (see below). When path C is a pathway, however, **23** would be a more likely intermediate than **22** as backside bonding from an exo direction is less obstructed than that from the endo direction.

Oxidation of *exo*-norbornylhydrazine (**1**) in *tert*-butyl alcohol-*O*-*d* to alkyldiimide **20** followed by base-catalyzed decomposition of the diimide *via* the unsymmetrically solvated carbanion **24** (Scheme I, path B) would yield *exo*-norbornane-d_1 (**5**). Entry into the **7x**–**7n** equilibrium also affords **5** and **6** (path A); similar pathways are available for **2**. Our data are again consistent with the intervention of two pathways, A and B. That path B intervenes is evidenced by the observation of 28% *endo*-norbornane-d_1 (**6**) in the cleavage of **2**. This alone does not implicate an intermediate such as **25** in the cleavage of **2**. The *endo*-norbornane-d_1, however, does not arise by way of the **7x**–**7n** equilibrium since exclusive exo capture is observed under conditions producing nearly complete racemization in the case of the 2-phenyl-2-butyl system (see below). The relatively large amount of *endo*-norbornane-d_1 observed in the cleavage of **2** is surprising considering the sterically crowded situation present at the endo face in **25**.

When *p*-toluenesulfonhydrazides **3** and **4** were subjected to basic cleavage, under which conditions in which the 2-phenyl-2-butyl system afforded nearly complete racemization, only *exo*-norbornane-d_1 (**5**) was isolated. These results are best explained by base-catalyzed decomposition of diimides **20** and **21** followed by entry into the **7x**–**7n** equilibrium. It is highly unlikely that *exo*-norbornane-d_1 is formed by a retention mechanism in the cleavage of **3** and an inversion mechanism in the cleavage of **4** since they were cleaved under *identical* conditions. *Capture exclusively* from the exo face (within the limits of the experiment) could reflect the position of the **7x**–**7n** equilibrium or could indicate that a steric preference for exo capture dominates the reaction.

The radical decomposition of **20** and **21** produced



from **1** and **2** afforded an identical (within experimental error) mixture of products, 89% *exo*- and 11% *endo*-norbornane-d_1. These results are in agreement with other observations of the 2-norbornyl radical in which only a modest selectivity for exo capture was observed.[19]

The results show an overwhelming tendency for exo capture of the 2-norbornyl anion. Two facts are of consequence: (1) the generation of a 2-norbornyl anion by a method known to effect nearly complete racemization in the 2-phenyl-2-butyl system affords an exo:endo ratio of >97:3; and (2) the pathways available for the cleavage reactions are dependent on the solvent employed. The predominance of exo product under all conditions is in general agreement with the results of deuterium exchange reactions of 2-norbornanones[7-9] and the exo capture by deuterium of the norbornyl anion derived from carbon–carbon cleavage of the homoenolate anion.[20] In the latter case, it appears now that the capture of the norbornyl anion from the exo side in alkaline medium is primarily sterically controlled rather than being a result of the position of the leaving group.

Experimental Section[21]

exo-**Norbornylamine Hydrochloride (12).** This amine was prepared according to a reported method and isolated as the hydrochloride to yield 86.5% of product: mp 320–323° dec (not hygroscopic) (lit.[22] mp 316–320° dec, hygroscopic); ir (mull) 1610 cm^{-1} (C–N); nmr (D_2O) δ 1.45 (m, 8,C-3,5,6,7 H) 2.38 (m, 2, C-1,4 H), 3.12 (m, 1, C-2 H).

N-(*exo*-**Norbornyl)aminoacetonitrile Hydrochloride (13).** A solution of 44.3 g (0.30 mol) of **12**, 50 ml of water, 50 ml of ether, 50 ml of isopropyl alcohol, and 24.2 ml (0.30 mol) of a 37.2% formaldehyde solution was maintained at 0.5° and treated dropwise over 30 min with a solution of 19.2 g (0.30 mol) of potassium cyanide in 50 ml of water.[23] After 24 hr, the ethereal layer was removed and the aqueous phase was extracted with two 50-ml portions of ether. The combined extracts were dried over magnesium sulfate, and the solution was saturated with anhydrous hydrogen chloride. The yield of white solid which precipitated was 44.0 g (0.24 mol, 78.7%): mp 220–221° (darkens 195°) (from ethanol–ethyl acetate); ir (mull) 2200 cm^{-1} (C–N), 1580 cm^{-1} (C–N); nmr (D_2O) δ 1.50 (m, 8, C-3,5,6,7 H), 2.52 (m, 2, C-1,4 H), 3.35 (m, 1, C-2 H), 4.21, (2, NCH_2CN).

Anal. Calcd for $C_9H_{15}N_2Cl$: C, 58.00; H, 8.05; N, 15.01. Found: C, 58.19; H, 7.90; N, 15.26.

N-**Nitroso-***N*-(*exo*-**norbornyl)glycine (14).** A solution of 20.0 g (0.11 mol) of *N*-(*exo*-norbornyl)aminoacetonitrile hydrochloride, 15.0 g (0.25 mol) of potassium hydroxide, and 30 ml of water was heated on a steam bath for 12 hr. The solution was evaporated to remove ammonia, acidified to pH 2, cooled to 0°, and treated dropwise over 3–4 hr with 8.0 g (0.11 mol) of sodium nitrite in 15 ml of water. On refrigeration a large amount of white solid was obtained. Repeated nitrosation and refrigeration yielded 16.6 g (0.084 mol, 76.4%) of a white solid: mp 119–120° (from water); ir (mull) 3000–2700 cm^{-1} broad (COOH), 1750 cm^{-1} (C=O acid), 1360 cm^{-1} (NO); nmr ($CDCl_3$) δ 1.70 (m, 8, C-3,5,6,7 H), 2.41 (broad, 1, C-4 H), 2.79 (broad, 1, C-1 H), 4.10 (m, 1, C-2 H (endo)).

Anal. Calcd for $C_9H_{14}N_2O_3$: C, 54.60; H, 7.07; N, 14.13. Found: C, 54.60; H, 7.28; N, 14.27.

exo-**Norbornylsydnone (15).** A suspension of 10.0 g (0.05 mol) of *N*-nitroso-*N*-(*exo*-norbornyl)glycine in 50 ml of dry methylene chloride was treated slowly with 60 ml of trifluoroacetic anhydride.[24] The mixture was heated to the reflux temperature for 15 hr and then the volatile materials were evaporated. The dark oil residue was dissolved in dry methylene chloride and subjected to column chromatography on a 4 ft × 0.50 in. column of Merck alumina. On evaporation of the solvent, a light tan solid was obtained which weighed 7.0 g (0.039 mol, 77.8%): mp 45–46°; ir (melt) 3210 cm^{-1} (CH sydnone), 1750 cm^{-1} (C=O sydnone); nmr (CCl_4) δ 1.60 (m, 8, C-3,5,6,7 H), 2.50 (broad, 1, C-4 H), 2.75 (broad, 1, C-1 H), 4.47 (m, 1, C-2 H) (endo)), 6.62 (s, 1, sydnone H).

Anal. Calcd for $C_9H_{12}N_2O_2$: C, 60.00; H, 6.67; N, 15.55. Found: C, 60.00; H, 6.70; N, 15.59.

exo-**Norbornylhydrazine Oxalate (16).** A solution of 17.5 g (0.097 mol) of *exo*-norbornylsydnone and 32 ml of concentrated hydrochloric acid was heated on a steam bath for 2 hr after which time gas evolution had ceased. The acidic solution was neutralized with a 25% sodium hydroxide solution while being kept at ~5° and was extracted with eight 50-ml portions of ether. The combined extracts were dried over potassium carbonate and filtered into a solution of 15.0 g of oxalic acid dihydrate in 100 ml of 95% ethanol. After refrigeration for 16 hr the solid was collected by filtration and recrystallized from methanol–ethanol (9:1) to yield 9.5 g (0.044 mol, 45.4%) of light tan crystals: mp 174–175°; nmr (D_2O) δ 1.40 (m, 8, C-3,5,6,7 H), 2.43 (m, 2, C-1,4 H), 3.17 (m, 1, C-2 H (endo)).

Anal. Calcd for $C_9H_{16}N_2O_4$: C, 50.00; H, 7.41; N, 12.95. Found: C, 50.04; H, 7.60; N, 12.76.

1-(*exo*-**Norbornyl)-2-***p*-**toluenesulfonhydrazide (3).** To a solution of 2.3 g of potassium hydroxide in 28 ml of water was added 3.9 g (0.0166 mol) of *exo*-norbornylhydrazine oxalate. The solution was shaken vigorously and extracted with three 50-ml portions of ether which were combined and dried with anhydrous potassium carbonate for 3 hr. The drying agent was removed by filtration, 1.4 g (0.0139 mol) of triethylamine was added, and the solution was cooled in an ice bath as 2.6 g (0.0139 mol) of *p*-toluenesulfonyl chloride was added. After allowing the solution to cool for 24 hr, the white precipitate of triethylamine hydrochloride was removed by filtration. The filtrate was concentrated on a rotary evaporator until crystals began to form. Cooling and filtration yielded 0.65 g (0.0023 mol, 14.0% based on oxalate) of light tan crystals: mp 116–118°; ir (mull) 3400–3100 cm^{-1} (NH), 1580 cm^{-1} (C–N); nmr ($CDCl_3$) δ 1.20 (m, 8, C-3,5,6,7 H), 2.12 (m, 2, C-1,4 H), 2.41 (s, 3, $ArCH_3$), 2.77 (m, 1, C-2 H (endo)), 5.55 (s, 2, NH), 7.50 (q, 4, ArH).

Anal. Calcd for $C_{14}H_{20}N_2O_2S$: C, 60.00; H, 7.14. Found: C, 59.50; H, 7.12.

endo-**Norbornylhydrazine (2).** A solution of 20.5 g (0.17 mol) of norcamphor hydrazone,[25] 50 mg of platinum oxide catalyst, 50 mg of gelatin, and 100 ml of absolute ethanol was placed in a pressure bottle on a Paar low-pressure hydrogenation apparatus. Hydrogen uptake at 50 psi (average) continued for 14 days. The solution was then treated with charcoal, filtered, and distilled at reduced pressure to yield 10.0 g (0.079 mol, 46.4%) of a clear liquid: bp 80–82° (4–4.5 mm); ir (neat) 3500–3100 cm^{-1} (NH), 1650 cm^{-1} (C=N); nmr ($CDCl_3$) δ 1.45 (m, 8, C-3,5,6,7 H), 2.15 (m (broad), 1, C-4 H), 2.33 (m, (broad), 1, C-1 H), 3.00 (m, 1, C-2 H) (exo)), 3.23 (s (broad), 3, NH).

(19) R. Bartlett, G. Fickes, F. Haupt, and R. Helgeson, *Accounts Chem. Res.*, **3** 177 (1970).

(20) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **88**, 3354 (1966).

(21) Nmr spectra were recorded with a Varian A-60 spectrometer. Vpc analysis and isolation of products were performed with a Varian 1520 C chromatograph employing a 10-ft by 0.50-in. column of SE-30 (30%) on Chromsorb W. Mass spectra were obtained from Dr. M. E. Freeburger at Wright-Patterson AFB, Ohio, and on a Hitachi RMU-6 instrument at the University of Iowa.

(22) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *J. Amer. Chem. Soc.*, **85**, 169 (1963).

(23) N. Zelinsky and B. Arzibachoff, *Ber.*, **40**, 3053 (1907).

(24) H. Daeniker and J. Druey, *Helv. Chim. Acta*, **40**, 918 (1957).

(25) K. Alder, H. Wirtz, and H. Koppelberg, *Justus Liebigs Ann. Chem.*, **601**, 138 (1956).

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.

(26) G. Zweifel and H. C. Brown, *Org. React.*, 13, 1 (1963).
(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]

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 *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).
(3) M. Hanack and H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, 6, 666 (1967).