(50%, 300 ml) was added; the mixture was refluxed for an additional 6 hr and then extracted with ether. The ether layer was washed with water, dried over potassium carbonate, and freed of ether by evaporation. Preparative glpc (column B) afforded material with a retention time identical with that of the Wolff–Kishner product from **4**. The product displayed an nmr band at 0.90 (d) ppm which is not present in the spectrum of pure **8**. The area ratio of the band at 0.90 to the one at 1.05 was 11 : 20.

Solvolysis of 3. A small amount of **3** was added to 5 ml of solvent in a small vial and placed in a water bath at the indicated temperature. After the desired reaction time (15–30 min), the contents were added to 5 ml of ether and cooled. The mixture was basified with a few drops of 50% sodium hydroxide and separated. The aqueous layer was extracted with 3 ml of ether. The combined, dried ether layer was concentrated to *ca.* 1 ml on a rotary evaporator. This material was then analyzed by glpc (column B). A control run with **3** showed that 70–85% of **3** and/or **4** was recovered.

Acknowledgment. We are grateful to the National Science Foundaton, Eli Lilly and Co., and the Graduate School of the University of Wisconsin—Milwaukee for support of this work. We also thank Benjamin Adams for obtaining some of the nmr data.

Bridged Polycyclic Compounds. LXXVI. The Nature of the Norbornenyl–Nortricyclyl Cation[1]

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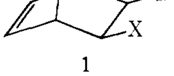
Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302. *Received January 4, 1973*

Abstract: *exo*-3-Deuterio-*exo*-2-norbornenyl *p*-bromobenzenesulfonate (**1**-OBs) acetolyzes, under a wide variety of conditions, to give, in addition to deuterionortricyclyl acetate (**3**-OAc), *equal* quantities of *exo*-3-deuterio-*exo*-2-norbornenyl acetate (**1**-OAc) and of the Wagner–Meerwein rearrangement product, *syn*-7-deuterio-*exo*-2-norbornenyl acetate (**2**-OAc). This finding removes the necessity for consideration of any unsymmetrical norbornenyl–nortricyclyl cation, as has been proposed earlier by others. Heating *exo*-3-deuterio-*exo*-2-norbornenyl thiocyanate (**1**-SCN) in sulfolane gives a mixture of *exo*-3-deuterio-*exo*-2-norbornenyl isothiocyanate (**1**-NCS) and *syn*-7-deuterio-*exo*-2-norbornenyl isothiocyanate (**2**-NCS), with the latter in slight excess, along with **2**-SCN. These results are discussed briefly.

Some time ago, we reported[2] that acetolysis of *exo*-3-deuterio-*exo*-2-norbornenyl *p*-bromobenzenesulfonate (**1**-OBs) leads to equal quantities of 3-deuterio- (**1**-OAc) and 7-deuterionorbornenyl acetate (**2**-OAc), in addition to deuterionortricyclyl acetate (**3**-OAc). Furthermore, we reported that acetolysis of **1**-OBs is accompanied by substantial deuterium scrambling, resulting in the formation of **2**-OBs. These observations led us to conclude that ionization of the carbon–oxygen bond gives an ion pair in which the cation is best represented as **4**, and that our evidence excluded the possibility[3] of a relatively stable unsymmetrical cation such as **5**, which suffers capture before complete rearrangement to its enantiomer or delocalization of the 1,2 bond to produce **4**.



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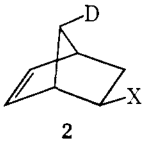

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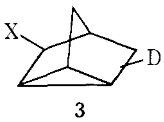

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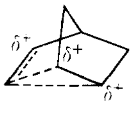

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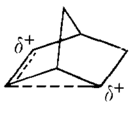

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Cation **5** was proposed originally to explain certain ^{14}C results which we therefore assumed to be incorrect. Recently Lee and Hahn[4] reported that acetolysis of 2-*endo*-deuterio-2-*exo*-norbornenyl *p*-bromobenzenesulfonate (**6**-OBs) at 14 or 24° (the latter being the temperature at which the previous work in this laboratory was conducted) leads to complete Wagner–Meerwein scrambling of the deuterium label between C-2 and C-1 (*i.e.*, to give equimolar amounts of **6**-OAc and **7**-OAc), thus confirming the presence of the symmetrical cation **4** (or its equivalent) in the solvolysis. However, they also reported that at 45 and at 65°, scrambling was not complete, **6**-OBs giving substantially more **6**-OAc than **7**-OAc, consistent with the ^{14}C results. We have now done acetolyses of **1**-OBs at temperatures from 24 to 65°, with initial concentrations of **1**-OBs varying from 0.03 to 0.48 *M*, and with potassium acetate or sodium acetate as base in initial concentrations 0.30–0.52 *M*, and have failed to observe product ratios of **1**-OAc to **2**-OAc differing significantly from unity (see Experimental Section).[5]

Professor Lee has kindly sent us material from Dr. Hahn's thesis and we find no errors in the calculations made from their data. We are presently unable to rationalize the discrepancies between our work and theirs.

In attempting to find conditions in which capture of intermediate cations might be anticipated to occur

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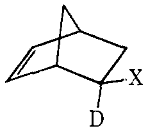
[1] Paper LXXV: F. R. Jensen, J. J. Miller, S. J. Cristol, and R. S. Beckley, *J. Org. Chem.*, 37, 4341 (1972).

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

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

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

[5] Again scrambling of **1**-OBs and **2**-OBs was observed, and, in addition, return was observed leading to **3**-OBs, such that experiments interrupted after about 90% solvolysis resulted in the isolation of most of the bromobenzenesulfonate as **3**-OBs. The composition was probably close to the equilibrium mixture of **1**-OBs, **2**-OBs, and **3**-OBs. Earlier experiments,[2] in which the sulfonate was isolated after about 10% solvolysis, did not show observable isomerization to **3**-OBs. Our present results thus require modification of the earlier statement[2] that "return from the **4**-OBs ion pair (produced from **1**-OBs) is too fast to allow significant migration of the *p*-bromobenzenesulfonate ion to C-5 to give **3**-OBs."



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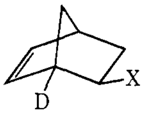

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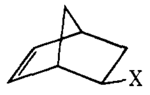

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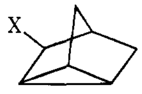

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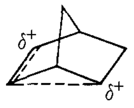
more rapidly (*i.e.*, at an early ion-pair stage) than that in solvolysis, we were attracted to the thiocyanate–isothiocyanate rearrangement.[6] Indeed Spurlock and Cox[7] have shown that isomerization of **8**-SCN leads to mixtures of isothiocyanates substantially richer in **8**-NCS than in **9**-NCS, while that of **9**-SCN leads to mixtures substantially richer in **9**-NCS than in **8**-NCS. Their interpretation was complicated by the assumption that the first ion pair (**10**) produced in rearrangement of **8**-SCN involved the unsymmetrical ion **5** rather than the symmetrical ion **4**, *e.g.*, the ion pair (**11**), while the ion pair produced from **9**-SCN was assumed to be **12**.



$\bar{S}CN$

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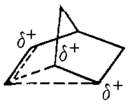
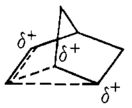


$\bar{S}CN$ $N\bar{C}S$

11



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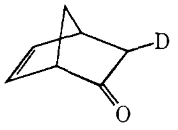
In any case, however, they demonstrated that the ion pair formed from **8**-SCN (**10** or **11**) collapsed to isothiocyanate product at a rate competitive with relaxation by anion migration and thus by equilibration to a mixture with **12**.[8]

This then offered a system in which one could attempt to capture **5**, if indeed it were formed, or failing that, increase confidence in our results on **1**-OBs acetolysis. As our correspondence with Professor Spurlock urging him to undertake a study with **1**-SCN was not fruitful, we decided to do this experiment ourselves. As described below, no evidence for the unsymmetrical cation **5** (or the ion pair **10**) was found.

Preparation of Materials. The synthesis of **1**-SCN which we chose involved, as the first step, the base-catalyzed deuteration of dehydronorcamphor. As has been reported,[9] there was formed a mixture containing largely **13**, admixed with a small amount of dideuteriodehydronorcamphor **14** and a lesser amount of undeuterated material. Analysis is given for the thiocyanate (**1**-SCN) below. While the Experimental Section gives precise data, for clarity the discussion is simplified by considering the material as **13** and its derivatives. Reduction of **13** with sodium borohydride[9,10] gave a mixture containing largely[10] **15**-OH, which was recrystallized to give **15**-OH in 70% yield; **15**-OH was converted to **15**-OBs. Spurlock and Cox[7] converted the undeuterated analog of **15**-OBs to **8**-SCN with tetraethylammonium thiocyanate in acetone in a sealed tube, which produced **8**-SCN admixed with **8**-NCS, **9**-SCN, and **9**-NCS. We found it more convenient to use potassium thiocyanate in hexamethylphosphoramide. This gave a product, containing 93% of **1**-SCN, 7% of **3**-SCN, and a trace of deuteriodehydronorbornenyl isothiocyanate, from which pure **1**-SCN could be readily separated. Mass spectral analysis showed 2.4% d_0, 84.7% d_1, and 12.8% d_2 (**8**-SCN, **1**-SCN, and **16**-SCN) in the product. Results on such a mixture are easily calculable (see Experimental Section). Use of KSCN in hexamethylphosphoramide thus was largely a direct displacement process, although the formation of **3**-SCN was probably due to intervention of **4**.[11]



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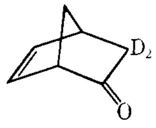

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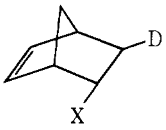

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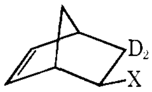

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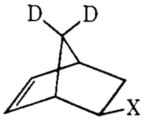

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Isomerization Experiments. When **1**-SCN was heated in sulfolane at 146°, isomerization occurred readily, as expected.[7] Reaction mixtures contained **1**-SCN, **2**-SCN, **3**-SCN, **1**-NCS, **2**-NCS, and **3**-NCS. Aliquots were removed from time to time, worked up as described by Spurlock and Cox,[7] and analyzed by gas chromatography. These results are given in Table I.

Table I. Isomerization of 0.1 *M* *exo*-3-Deuterio-*exo*-2-norbornenyl Thiocyanate (**1**-SCN) in Sulfolane at 146°[a]

	% of mixture			
Time, hr	1-SCN + 2-SCN	1-NCS + 2-NCS	3-SCN	3-NCS
0	100.0	0	0	0
7.25	67.9	21.8	4.9	5.4
11.50	59.0	26.3	6.4	8.4
26.75	32.3	40.2	12.2	15.3
35.25	24.1	47.2	11.6	17.2
48.00	16.2	49.7	14.4	19.2

[a] Glpc analysis.

The unsaturated thiocyanates and isothiocyanates were isolated by preparative gc and analyzed by mass spectrometry. The principal mode of cleavage in these dehydronorbornenyl derivatives is the retro-Diels–Alder process,[2,12] so that the sum of deuterium atoms on C-2 and C-3 can be distinguished readily from that of those on C-1, C-4, C-5, C-6, and C-7, by measurement of the $C_5H_{6-n}D_n$ radical cation peak intensities. We, of course, are mechanistically limited to C-3 and C-7 interchange. Results of the mass spectral analyses are given in Table II.

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[6] For reviews see (a) A. Fava in "Organic Sulfur Compounds," Vol. II, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, Oxford, 1966, pp 73–91; (b) L. A. Spurlock and T. E. Parks in "Mechanisms of Reactions of Sulfur Compounds," Vol. III, N. Kharasch, Ed., Interscience Research Foundation, Santa Monica, Calif., 1968, pp 161–168.

[7] L. A. Spurlock and W. G. Cox, *J. Amer. Chem. Soc.*, **93**, 146 (1971).

[8] Our work with *p*-bromobenzenesulfonate return (this paper and ref 2) in the conversion of **1**-OBs to its mixture with **2**-OBs faster than conversion to **3**-OBs is analogous.

[9] P. Barraclough and D. W. Young, *Tetrahedron Lett.*, 2293 (1970).

[10] H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, **88**, 2811 (1966).

[11] When **8**-OBs or **9**-OBs was treated under these conditions, the product was principally **9**-SCN, admixed with **8**-SCN and **9**-NCS. These products suggest that a cationic process was involved.

[12] S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2738 (1966), and references therein.

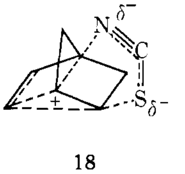
Table II. Mass Spectral Data on Deuterionorbornenyl Thiocyanates and Isothiocyanates from Isomerization of **1**-SCN in Sulfolane at 146°

Time, hr	% in RSCN[a,b]			% in RNCS[b]			Nominal % in mixture[c]			
	$C_5H_6\cdot^+$	$C_5H_5D\cdot^+$	$C_5H_4D_2\cdot^+$	$C_5H_6\cdot^+$	$C_5H_5D\cdot^+$	$C_5H_4D_2\cdot^+$	**1**-SCN:**2**-SCN		**1**-NCS:**2**-NCS	
0	99.6	0.4					99.6	0.4		
7.25	86.8	11.7	1.5				86.0	14.0		
11.50	80.2	17.6	2.2	45.7	47.3	7.0	78.7	21.3	44.4	55.6
26.75	68.4	27.8	3.9	47.4	45.7	6.9	67.0	33.0	46.1	53.9
35.25	65.3	30.4	4.3	47.2	45.9	6.8	64.0	36.0	46.0	54.0
48.00	62.9	32.4	4.6	47.0	46.0	7.0	61.6	38.4	45.8	54.2
96.00				47.7	45.4	6.8			46.5	53.5

[a] The parent RSCN ion had 2.4 ± 0.2% d_0, 84.7 ± 0.6% d_1, and 12.8 ± 0.6% d_2 species with all of the label at C-3. [b] Complete scrambling of deuterium between C-3 and C-7 should lead to values of 51.2, 42.3, and 6.4 for d_0, d_1, and d_2 species of $C_5H_{6-n}D_n$ radical cations. [c] Data fit to assumption that all starting material was **1**-SCN.

The data in Table I are reasonably consistent (products and rate) with the data on the undeuterated compound **8**-SCN reported earlier,[7] although we find somewhat less **3** isomers than they report. The deuterium scrambling (**1**-SCN→**2**-SCN) proceeds at a rate about equal to the thiocyanate to isothiocyanate isomerization, so that, of the **1**-SCN molecules which react, 30% rearrange to **2**-SCN and, assuming that, to a first approximation, a symmetrical intermediate(s) is (are) involved, 30% return to **1**-SCN, 30% isomerize to **1**- and **2**-NCS, and about 10% rearrange to **3**-SCN and **3**-NCS. Slightly preferred capture of cations by the sulfur atom of the thiocyanate ion rather than by the nitrogen atom is similar to that observed[13] for norbornyl cation.

The purpose of this investigation was, of course, to look for evidence for intermediacy of an unsymmetrical species such as **5** (*e.g.*, the ion pair **10**), which might be captured before isomerization to the symmetrical ion **4** (*e.g.*, **11**). Such an intermediate would result in the formation of more **1**-NCS than **2**-NCS. The data in Table II show that just the opposite is true. The first set of data (11.5 hr) shows a ratio of **2**-NCS to **1**-NCS of 1.25 to 1.0, and after more deuterium scrambling has occurred in the thiocyanate, this ratio is reduced to 1.15 to 1.0. This excess labeling at C-7 appears to be outside of experimental error and, would appear, besides removing any further need to consider the unsymmetrical ion **5** in the norbornenyl-nortricyclyl system, to require another mechanism for the thiocyanate-isothiocyanate interconversion in which **1**-SCN goes directly to **2**-NCS, accounting for about 10% of the overall reaction. Spurlock and Parks[13] considered a concerted process for the norbornyl systems (the analogous suggestion is pictured in **18**), as has been observed with allylic systems,[14] although they rejected this process for their system. Perhaps such a process, or an unsymmetrical ion pair (**19**) in which the thiocyanate ion reacts at the nitrogen atom before relaxation, is involved. Lack of information makes further speculation regarding this unwarranted.



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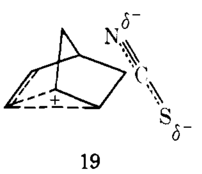

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Experimental Section

Pmr spectra were taken on a Varian Associates A-60A spectrometer. Mass spectra were taken on Varian Atlas CH-5 and CH-7 mass spectrometers using a combination of multiple scans and/or slow scanning of certain regions. Analyses were done at 70 eV and/or 15 eV. Calculations were often simpler for the lower ionizing energy, where fragmentation patterns were generally simpler. Aerograph A-90-P3 and A-700 gas chromatographic equipment was used for analytical and preparative separations, respectively. The analyses were conducted using 1.5% Carbowax on Chromosorb W (for acetates[2]) or 15% diethylene glycol succinate on Chromosorb W (for thiocyanates and isothiocyanates[7]).

***exo*-3-Deuterio-*exo*-2-norbornenyl *p*-bromobenzenesulfonate** (**1**-OBs), mp 179–181°, was prepared as described previously.[2] Mass spectral analysis[12] on the sample of **1**-OH derived from the same sample as the **1**-OBs indicates that this material was 86.5 ± 0.5% **1**-OBs, 12.5 ± 0.5% **8**-OBs, and 1.0% **2**-OBs.

Acetolyses were conducted in reagent grade acetic acid which had been heated at reflux with 2% acetic anhydride for 24 hr and which contained sodium or potassium acetate that had been dried at 120° for 24 hr and then stored in a desiccator. The solutions of **1**-OBs containing alkali acetate in acetic acid were heated in constant-temperature baths for approximately 11 hr at 24°, 1.0 hr at 45°, and 24 min at 65°. The solutions were worked up as described previously.[2] After most of the extraction solvent (pentane) was removed by distillation, the solution was cooled to −30° and the *p*-bromobenzenesulfonate, which was largely 3-OBs, was allowed to crystallize. Removal of the remaining pentane gave a mixture of acetates which were analyzed as described before.[2,12] Results are given in Table III.

***exo*-3-Deuterio-2-dehydronorcamphor** (**13**) was prepared by treatment of dehydronorcamphor with sodium deuteroxide in deuterium oxide–dioxane, following the procedure of Barraclough and Young,[9] and was reduced with sodium borohydride as described by Brown and Muzzio.[10] Recrystallization from pentane gave a 70% yield of *exo*-3-deuterio-*endo*-2-norbornenyl alcohol (**15**-OH) which was converted to **15**-OBs with *p*-bromobenzenesulfonyl chloride in pyridine. Pmr analysis of the **15**-OH sample showed no absorption for the 3-exo proton.

***exo*-3-Deuterio-*exo*-2-nonbornenyl Thiocyanate** (**1**-SCN). A solution of 4.0 g (40 mmol) of potassium thiocyanate and 2.0 g (6.0 mmol) of the **15**-OBs described above in 20 ml of hexamethylphosphoramide (distilled from calcium hydride and stored over molecular sieves) was heated at 81° for 48 hr, cooled, and poured into 50 ml of water. The resulting mixture was extracted with three 10-ml portions of *n*-pentane. The pentane extracts were washed with two 20-ml portions of water and dried over anhydrous $MgSO_4$. The pentane was evaporated and the residue was distilled (80–85° at 1.5 Torr). Glpc analysis showed 93% **1**-SCN, 7% **3**-SCN, and a trace of deuterated **8**-NCS. Preparative glpc gave 0.60 g (60%) of **1**-SCN. Mass spectral analysis showed 2.4 d_0, 84.7 d_1, and 12.8 d_2 species present with less than 0.4% deuterium in the $C_5H_6\cdot^+$ fragment.

Isomerizations of 1-SCN. Aliquots of a 0.1 *M* **1**-SCN solution in sulfolane were sealed in glass tubes at about 1-Torr pressure. The sample size was varied so as to give at least 10 mg of each olefin isomer after partial isomerization; *i.e.*, the first and last samples contained more solution. The tubes were removed at different time intervals, worked up and analyzed as described by Spurlock.[7] The data given in Table II assume identical thermal conductivity responses for isomers. Samples of each olefin were separated by glpc and analyzed by mass spectrometry. Multiple

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(13) L. A. Spurlock and T. E. Parks, *J. Amer. Chem. Soc.*, **92**, 1279 (1970).

(14) (a) P. A. Smith and D. W. Emerson, *ibid.*, **82**, 3076 (1960); (b) A. Ilecito, A. Fava, and U. Mazzucato, *Tetrahedron Lett.*, No. **11**, 27 (1960).

Table III. Product Compositions of Deuterio-2-*exo*-norbornenyl Acetate from Acetolysis of 3-*exo*-Deuterio-2-*exo*-norbornenyl *p*-Bromobenzenesulfonate (**1**-OBs)[a] under Various Conditions

[1-OBs], *M*	[NaOAc], *M*	[KOAc], *M*	Temp, °C	% D at C-7	Total % D	% rearrangement
0.48		0.52	24	44.0	88.4	49.8[b]
0.03	0.30		24	41.2	85.3	48.4[b]
0.48		0.52	45	44.9	85.7	52.4[b]
				43.4	85.2	50.9[c]
0.03	0.30		45	45.6	85.6	53.3[b]
				44.7	88.2	50.7[c]
0.03		0.52	45	40.6	85.5	47.5[b]
				44.5	87.6	50.8[c]
0.48		0.52	65	43.2	84.6	51.1[b]
				43.3	85.1	50.9[c]
0.03	0.30		65	44.1	88.7	49.7[b]
				45.1	88.5	51.0[c]

[a] Mass spectrometer analysis on starting material indicated starting material was 86.5 ± 1.0% **1**-OBs, 12.5% **8**-OBs, and 1.0% **2**-OBs, but each determination of % rearrangement was calculated using individual data points for total D content. [b] Analysis at 15 eV. [c] Analysis at 70 eV.

scans of data at 15 eV (inlet temperature 120°) were averaged to give the data in Table II.

Treatment of Mass Spectral Data. The starting nominal **1**-SCN was a mixture containing 2.4% **8**-SCN, 84.7% **1**-SCN, and 12.8% **16**-SCN, with less than 0.5% of **2**-SCN and **17**-SCN. Any reaction which proceeds through a symmetrical intermediate, *e.g.*, **4**, which is captured equally well at C-1 and C-2, would lead to a product mixture containing 2.4% of **8**-X, 42.3% of **1**-X, 42.3% of **2**-X, 6.4% of **16**-X, and 6.4% of **17**-X. Such a mixture would have the analysis *m/e* 66:67:68 (after isotope abundance correction) of 51.2:42.3:6.4. Therefore the nominal value for **2**-X, that is, the value which would have been obtained if the starting material had been pure **1**-X, is calculated as **1**-d_0/102.4, and an independent value for **2**-X is given by d_1/84.7 where d_0 and d_1 are observed percentages of undeuterated and monodeuterated species. (In principle, the amount of scrambled deuterium can also be calculated from the data for the d_2 species, but in practice, these data have larger per cent errors and have been ignored.) The results given in Table II are the averages of the **1**-X:**2**-X ratios calculated in each way.

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Hydroboration. XXXIV. The Cyclic Hydroboration of 1,5-Hexadiene with Borane in Tetrahydrofuran and 9-Borabicyclo[3.3.1]nonane. A New Convenient Route to the Borepane Ring System Utilizing 9-Borabicyclo[3.3.1]nonane

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Abstract: Confirming evidence is presented for the formation of a mixture of 3:2 dumbbell-shaped compounds in the hydroboration of 1,5-hexadiene with borane in tetrahydrofuran in the molar ratio of 3:2. Oxidation of the products provides 1,6-, 1,5-, and 2,5-hexanediols in a ratio of 72:22:6. Evidence is presented for the facile conversion of the boracycloheptyl ring moiety to the 2-methylboracyclohexyl moiety in the distillation or thermal treatment of the 3:2 products. The reaction of the 3:2 products or thermally treated 3:2 products with an equimolar quantity of borane in tetrahydrofuran provides mixtures containing predictable ratios of borepane and 2-methylborinane. Alternative methods for the preparation of the *B*-methoxy derivatives of these compounds are described. Evidence is presented that the reaction of 1,5-hexadiene with borane in a 1:1 molar ratio proceeds through the initial formation of the 3:2 product, followed by the subsequent reaction of this product with borane. The thermal treatment at 70° of the initial 1:1 hydroboration products provides a 78% yield of borepane and 2-methylborinane in a ratio of 70:30. The boracycloheptane ring is relatively stable in THF in the absence of borane, but in its presence the ring system undergoes a slow reaction involving opening of the ring. Thus the stability of the boracycloheptane ring appears to lie between the stabilities of the boracyclopentane and boracyclohexane rings. The hydroboration of 1,5-hexadiene with 9-borabicyclo[3.3.1]nonane (9-BBN) followed by treatment with borane in tetrahydrofuran provides a new synthesis of the boracycloheptyl ring system uncontaminated by isomeric boracyclanes. The method holds promise for the ready synthesis of boracyclanes in high yield and purity.

The hydroboration of 1,5-hexadiene with borane (or diborane) in the stoichiometric ratio 3:2 has been investigated previously by several workers.[2] Although some confusion had persisted regarding the

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(2) (a) K. A. Saegebarth, *J. Amer. Chem. Soc.*, **82**, 2081 (1960); (b) G. Zweifel, K. Nagase, and H. C. Brown, *ibid.*, **84**, 183 (1962); (c) B. M. Mikhailov, L. S. Vasil'ev, and E. Safonva, *Dokl. Akad. Nauk SSSR*, **147**, 630 (1962); (d) L. I. Zakharkin and A. I. Kovredov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 357 (1962); (e) L. I. Zakharkin and A. I. Kovredov, *ibid.*, 106 (1969).