^{13}C NMR Spectra of the Products of Hydroboration of 1-Alkynes and of 1-Halo-1-alkynes with 9-Borabicyclo[3.3.1]nonane and with Dicyclohexylborane. Investigation of the Thermal Decomposition of Some (1-Halo-1-alkenyl)dicyclohexylboranes

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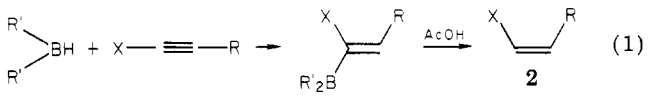
^{13}C NMR spectra were obtained (1) of 1-alkenylboranes and 1,1-diboraalkanes, the products of mono- and dihydroboration of 1-alkynes, respectively, and (2) of (1-halo-1-alkenyl)dialkylboranes, the products of hydroboration of 1-halo-1-alkynes with the title compounds. The chemical shift for C-1 of each 1,1-diboraalkane is reported. The products of the reactions of 9-borabicyclo[3.3.1]nonane with 1-halo-1-alkynes show upfield shifts (~10 ppm) for the alkene C-2 upon changing the solvent from $CDCl_3$ to THF. This indicates formation of an organoborane–THF complex, which is cited as the reason for slower protonolysis in THF solvent. The corresponding dicyclohexylborane products show much smaller ^{13}C shifts and undergo protonolysis rapidly in either $CDCl_3$ or THF solvent. With the dicyclohexylborane products, a cyclohexyl group migrates slowly at room temperature to give, after AcOH protonolysis, the 1-cyclohexyl-1-alkene.

Introduction

Previous work in this laboratory involved developing practical procedures for the synthesis of *cis*-1-halo-1-alkenes from 1-halo-1-alkynes (eq 1).[1] Representative (1-

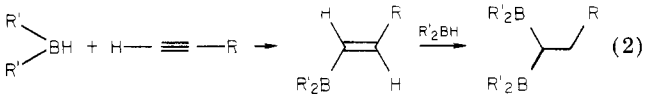


(1)

halo-1-alkenyl)dialkylboranes (1) were synthesized from dicyclohexylborane (Chx_2BH) and from 9-borabicyclo-[3.3.1]nonane (9-BBN). To obtain a better understanding of the reactivity of these compounds toward protonolysis, the ^{13}C NMR spectra were examined. During the course of this work, an unexpected thermal rearrangement of 1 (R = Chx) was observed, and the products were identified by ^{13}C NMR. Spectra of the corresponding non-halogenated products are also reported here.

Results and Discussion

1-Alkenyldialkylboranes (3 and 4) and 1,1-Diboraalkanes (5 and 6). Hydroboration of 1-alkynes with dialkylboranes gives 1-alkenylboranes, which can often react further to give 1,1-dibora compounds (eq 2).[2,3] The

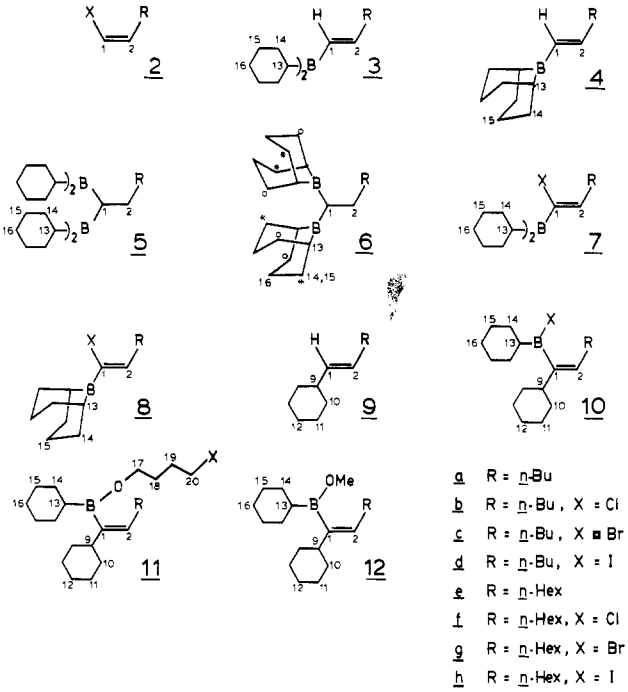


(2)

^{13}C shifts for 1-alkenylboranes 3 and 4 (Chart I) are included in Table I.

It is interesting to consider the effects of a boron substituent upon the carbon atoms in an adjacent single or double bond. For example, in Bu_3B, the ^{13}C shifts of C-1 and C-2 are 29.8 and 28.4 ppm, respectively.[4a] These could be compared to the shifts of C-4 (32.7 ppm) and C-5 (29.2 ppm) in 2-ethylheptane.[4b] (2-Ethylheptane was chosen to approximate the substitution pattern around boron.) Thus, there are only small upfield shifts at C-1 and C-2 upon replacement of carbon by boron. This might indicate a slight +I inductive effect of boron relative to carbon.[5] However, one should remember that the boron substituent effects in the example discussed above should not be

Chart I



(1) Brown, H. C.; Blue, C. D.; Nelson, D. J., unpublished results.
(2) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834. (b) Zweifel, G.; Clark, G. M.; Polston, N. L. *Ibid.* **1971**, *93*, 3395. (c) Brown, H. C.; Scouten, C. G.; Liotta, R. *Ibid.* **1979**, *101*, 96.
(3) Wang, K. K.; Scouten, C. G.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 531–6.
(4) (a) Yamamoto, Y.; Moritani, I. *J. Org. Chem.* **1975**, *40*, 3434. (b) Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **1971**, *43*, 1245–52. We are grateful to a referee for supplying this reference. (c) It should be noted that by comparing **3a** to **9a**, we are neglecting the effects of two alkyl substituents which are β to C-1 and γ to C-2. However, the error should be small, about −3 ppm at C-1 and ±1 ppm at C-2 (ref 5, p 75).
(5) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; Chapter 5.

0022-3263/83/1948-4538$01.50/0

Table I. ^{13}C NMR Shifts[a] of Organoboranes and of the Corresponding Products of Protonolysis or Rearrangement

	chemical shifts																			
compd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19	C-20
2b	117.5	131.3	26.4	30.2	22.0	13.4														
2c	107.6	135.0	29.5	30.4	22.3	13.9														
2d	82.1	141.3	34.4	30.1	22.2	13.9														
2f	118.0	131.9	27.2	29.0[c]	28.6[c]	31.8	22.8	14.1												
2g	107.6	135.0	29.8	28.9[c]	28.2[c]	31.7	22.6	14.0												
2h	82.1	141.3	34.7	28.8[c]	28.0[c]	31.7	22.6	14.0												
3a	133.4[b]	153.4	35.8	30.6	22.1	13.7							34.0[b]	27.5[c]	27.3[c]	26.9				
3e	133.3[b]	153.4	36.1	28.7[c]	28.4[c]	31.5	22.3	13.7					34.1[b]	27.5[d]	27.3[d]	26.9				
4a	134[b]	155.3	35.5	30.4	22.2	13.7							30[b]	33.5	23.7					
4e	134[b]	155.3	35.9	28.8[c]	28.2[c]	31.5	22.4	13.8					30[b]	33.5	23.7					
5a	44.7[b]	34.2	25.5	32.4	22.3	13.9							36.2[b]	27.6	27.6	27.0				
6a	55.3[b]	33.3	28.3	32.2	22.5	14.0							31.4[b]	33.3	33.0	23.1				
6e	55.4[b]	33.6	29.9[c]	29.1[c]	28.3[c]	31.8	22.5	13.9					31.4[b]	33.2	32.9	23.0				
7b	*b*	141.1	28.9	30.5	22.4	13.8							36.0[b]	27.6[c]	27.3[c]	26.9				
7c	*b*	135.3	31.4	30.6	22.3	13.8							35.7[b]	27.6	27.6	26.8				
7d	*b*	133.9	37.1	30.7	22.1	13.9							34.5[b]	28.9[c]	28.2[c]	26.8				
7f	*b*	141.0	29.2	28.9[c]	28.3[c]	31.6	22.5	13.9					35.8[b]	27.6[d]	27.3[d]	26.9				
7g	*b*	135.7	31.8	28.8[c]	28.4[c]	31.6	22.5	13.9					35.6[b]	27.6	27.6	26.8				
7h	*b*	134.0	37.3	28.6[c]	28.4[c]	31.6	22.5	13.9					34.4[b]	28.5[d]	27.8[d]	26.8				
8b	*b*	149.0	30.2	30.1	22.6	13.9							*b*	33.9	23.3					
8c	135[b]	151.5	33.4	30.0	22.6	13.9							32[b]	33.8	23.3					
8d	119[b]	156.4	39.4	29.8	22.5	14.0							33[b]	33.9	23.4					
8f	*b*	149.1	30.4	29.2[c]	28.0[c]	31.7	22.6	14.0					*b*	33.9	23.3					
8g	135[b]	151.5	33.7	29.1[c]	27.8[c]	31.7	22.6	14.1					32[b]	33.8	23.3					
8h	119[b]	156.4	39.8	29.1[c]	27.7[c]	31.7	22.6	14.1					33[b]	33.9	23.4					
9a	136.2	127.7	31.9[c]	32.3[c]	22.1	13.8			40.7	33.3	26.1	26.3								
9e	136.3	127.7	32.9	29.6[c]	28.8[c]	31.7	22.6	14.0	40.7	33.3	26.1	26.3								
10b	*b*	133.1	32.3[c]	32.2[c]	22.2	13.8			42.8	33.6	26.8[d]	26.2[e]	*b*	28.1[d]	27.4[d]	26.6[e]				
10c	*b*	131.7	32.2[c]	32.1[c]	22.2	13.9			42.5	33.7	26.9[d]	26.2[e]	*b*	28.7[d]	27.3[d]	26.5[e]				
10d	*b*	129.6	31.8[c]	32.2[c]	22.2	13.9			41.9	33.6	26.9[d]	26.1[e]	*b*	29.5[d]	27.0[d]	-				
10f	*b*	133.2	32.5	30.1[c]	28.8[c]	31.6	22.5	13.9	42.8	33.7	26.9[d]	26.2[e]	*b*	28.1[d]	27.4[d]	26.6[e]				
10g	*b*	131.9	31.8[c]	30.2[c]	29.0[c]	31.5	22.5	13.9	42.5	33.6	26.9[d]	26.2[e]	*b*	28.7[d]	27.3[d]	26.5[e]				
10h	*b*	129.7	32.6	29.5[c]	28.8[c]	31.6	22.5	13.9	41.9	33.6	26.9[d]	26.1[e]	*b*	29.5[d]	27.0[d]	26.4[e]				
11b	*b*	129.0	32.0[c]	32.4[c]	22.1	13.5			42.3	33.0	26.6[d]	26.0[e]	*b*	27.8[d]	27.5[d]	26.7[e]	65.8	29.1[f]	28.6[f]	44.2
11c	*b*	129.3	32.3[c]	32.6[c]	22.4	13.8			42.5	33.2	26.8[d]	26.3[e]	*b*	28.0[d]	27.8[d]	27.0[e]	65.9	33.1[f]	29.5[f]	30.0[f]
11d	*b*	129.0	32.0[c]	32.3[c]	22.1	13.6			42.2	33.0	26.6[d]	26.0[e]	*b*	27.7[d]	27.5[d]	26.7[e]	65.4	32.0[f]	30.0[f]	5.7
11f	*b*	129.7	33.2	30.4[c]	29.4[c]	32.0	22.8	14.0	42.9	33.5	27.1[d]	26.6[e]	*b*	28.3[d]	28.1[d]	27.3[e]	66.3	29.4[f]	29.7[f]	44.6
11g	*b*	129.0	32.6	29.7[c]	28.7[c]	31.4	22.1	13.4	42.2	32.9	26.5[d]	25.9[e]	*b*	27.7[d]	27.4[d]	26.6[e]	65.6	32.8[f]	29.7[f]	29.2[f]
11h	*b*	129.1	32.7	29.8[c]	28.8[c]	31.4	22.2	13.5	42.2	32.9	26.5[d]	26.0[e]	*b*	27.7[d]	27.5[d]	26.7[e]	65.4	32.0[f]	30.0[f]	5.8
12a	*b*	129.3	32.5[c]	32.4[c]	22.5	13.9			42.6	33.2	26.9[d]	26.3[e]	*b*	28.1[d]	27.8[d]	27.0[e]	54.8			
12e	*b*	129.4	32.9	30.1[c]	29.1[c]	31.7	22.5	13.9	42.6	33.2	26.9[d]	26.3[e]	*b*	28.0[d]	27.8[d]	27.0[e]	54.8			

[a] Parts per million downfield from internal Me_4Si; $CDCl_3$ solvent. [b] Signal broadened, often absent. [c–f] Interchangeable with same superscript.

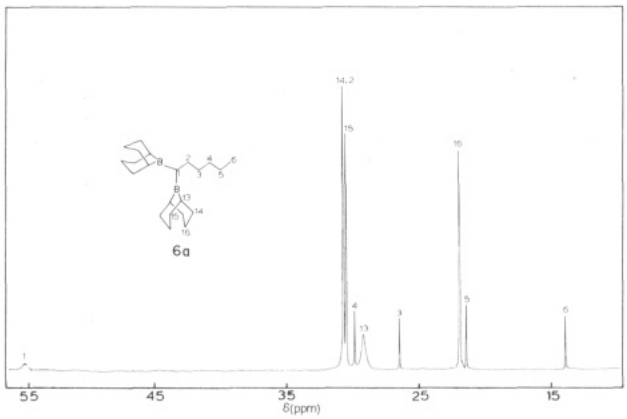


Figure 1. ^{13}C NMR spectrum of **6a** gives an example of prochirality (nonequivalence of C-14 and C-15). The signal for the dibora-substituted carbon (C-1) is observed easily.

considered general, and may be quite different for other organoboranes, especially those having other substituent patterns. The effect of a boron substituent upon a double bond is quite different. Comparison of the ^{13}C shifts of C-1 and C-2 in **3a** (133.4 and 153.4 ppm, respectively) with those in **9a** (136.2 and 127.7 ppm, respectively) show that relative to carbon, boron again causes only a small shift at C-1 but a rather large downfield shift at C-2. In particular, the large shift at C-2 (~25 ppm) implies significant π-bond conjugation, as previously observed.[4a,c] Thus, in these cases, the major effect of a boron substituent upon the adjacent double bond is probably a –K conjugative one.

The ^{13}C spectra of the 1,1-dibora compounds **5** and **6** are the first reported for this type of compound. The diboron-substituted carbons have chemical shifts in the general area expected considering the pattern of the adjacent substituents.[5,6] These carbons are easily observed, with linewidths at half-height similar to the monoboron-substituted alkane carbons (5–15 Hz). The signal for C-1 in the ^{13}C spectrum of **6a** (Figure 1) is typical.

In compounds **5** and **6**, there is no molecular symmetry plane which bisects a dicyclohexyl or 9-BBN group respectively. In particular, a plane containing a boron atom and the adjacent prochiral center(s), C-13, is not a plane of symmetry due to the substitution pattern at C-1. This leads to nonequivalence of the ring carbons β and γ to boron in **5** and β to boron in **6**.[7] This nonequivalence results in two well-separated signals in the ^{13}C spectrum of **6** (Figure 1; Chart I, * vs. o at C-14, -15).[8] There are two signals, rather than four due to rotation about the B–C-1 bond. The molecular symmetry plane through C-1 (also a prochiral center) causes the gem dialkylborane groups to be equivalent and, of course, is not responsible for the observed chemical nonequivalence within the 9-BBN group.[9] No similar doublets were observed in the spectrum of **5**. Apparently, in this case, there is accidental coincidence of the ^{13}C signals under the experimental conditions used in this investigation. For an excellent review and general discussion of prochirality and its effect on NMR spectra, see ref 7.

Hydroboration of 1-alkynes with dialkyboranes often results in mixtures of mono- and dihydroborated products.[3]

(6) Wrackmeyer, B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*, 227.
(7) Jennings, W. B. *Chem. Rev.* **1975**, *75*, 307.
(8) For another example see: Brown, H. C.; Soderquist, J. A. *J. Org. Chem.* **1980**, *45*, 846.
(9) We appreciate a referee informing us that similar chemical nonequivalence is observed in the ^{13}C NMR spectrum of 2,4,6-trimethylheptane. Carman, C. J.; Tarpley, A. R., Jr.; Goldstein, J. H. *Macromolecules* **1973**, *6*, 719–24.

Table II. ^{13}C NMR Shifts[a] of Selected Compounds in 1:1 $CDCl_3/THF_2$

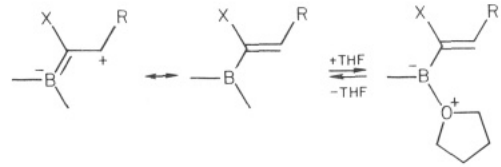
compd	chemical shifts C-1	C-2
3e	133.2[b]	153.6
4e	134[b]	153.2
7f, X = Cl	*c*	140.7
7g, X = Br	*c*	135.0
7h, X = I	*c*	133.5
8f, X = Cl	*c*	141.8
8g, X = Br	*c*	139.7
8h, X = I	130[b]	144.0
12e	*c*	129.6

[a] In ppm downfield from internal Me_4Si. [b] Broad signal. [c] Signal too broad to be observed.

The data in Table I show that ^{13}C NMR should be a convenient method for estimating the relative amounts of the two products.

(1-Halo-1-alkenyl)dialkylboranes (7 and 8). The boron-substituted alkene carbons (C-1) give very broad ^{13}C signals which are not always observed (Table I). Unlike 1-alkynes, the 1-halo-1-alkynes did not give any dihydroboration products, as determined by conventional methods.[1] This is in agreement with the ^{13}C NMR spectra. For comparison, the data for the analogous haloalkenes **2** are also given in Table I. Compounds **7** and **8** also seem to show downfield shifts at C-2, as in the nonhalogenated ones. However, the effect is difficult to measure as there appears to be a variable boron–halogen interaction. For **7**, the series Cl–Br–I gives increasingly upfield shifts at C-2, while for **8**, the opposite trend is observed.

When treated with AcOH, the 9-BBN compounds **8** protonolyze much more slowly in THF (20–30 h) than in noncomplexing solvents such as $CDCl_3$ or pentane (1–3 min). The slower reaction in THF is probably due to formation of a complex with the solvent (eq 3). This is



(3)

supported by the ^{13}C data for C-1 and C-2 (Tables I and II). The data for C-2 show a solvent shift of ~10 ppm upfield in THF, as compared to $CDCl_3$, for the 9-BBN hydroboration products.

In contrast, the dicyclohexylborane products **7** protonolyze rapidly (<1 min) in all solvents.[1] Comparison of the ^{13}C data for C-1 and C-2 of these compounds in $CDCl_3$ solvent (Table I) and in the presence of THF (Table II) shows only minor differences. This implies little if any complexation with THF. However, it is not clear why the 9-BBN adducts **8** strongly complex with THF while the corresponding dicyclohexylborane ones do not.

Stability of (1-Halo-1-alkenyl)dicyclohexylboranes (7). (1-Bromo-1-hexenyl)dicyclohexylborane **7c** slowly decomposes at room temperature in THF or nonpolar solvents (CCl_4, pentane). Therefore, if protonolysis (eq 1) is delayed, a new product is obtained, in addition to the desired *cis*-1-halo-1-hexene **2a**. This new product was identified as 1-cyclohexyl-1-hexene (**9a**) by comparison with authentic material prepared by a known synthesis.[10] A solution of **7c** in THF was kept at room temperature, and samples were quenched with AcOH and analyzed for

(10) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086.

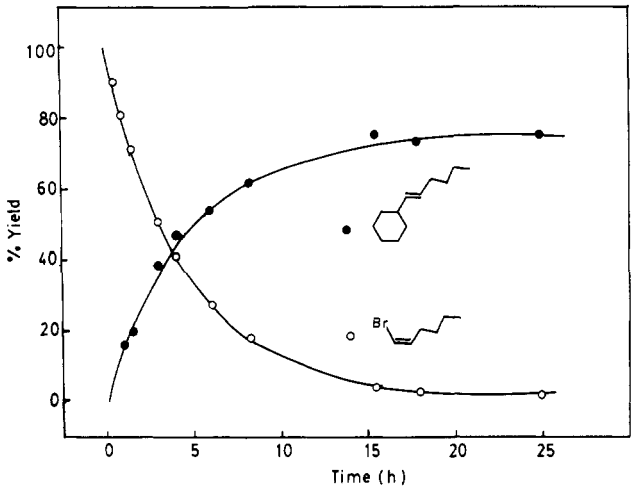
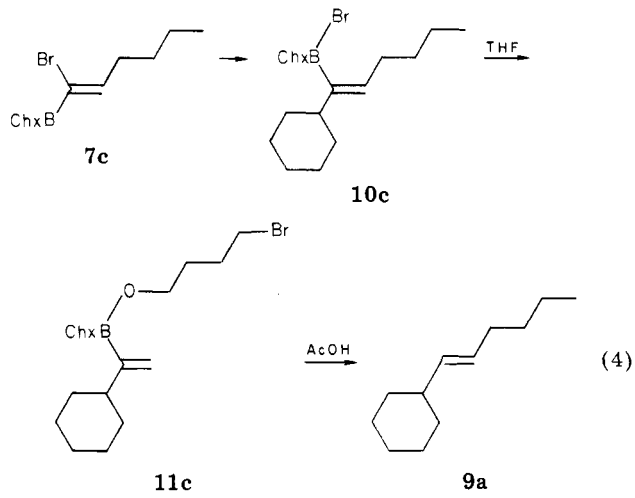


Figure 2. GC analysis of the room-temperature decomposition of **7c** in THF.

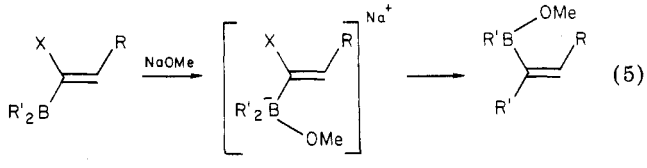
9a and **2a** to determine the rate of decomposition (Figure 2). Similar rates were obtained with CH_2Cl_2 solvent. The presence of **9a** after protonolysis implies an alkyl migration (eq 4), and NMR spectra consistent with the expected



intermediate **10c** were obtained. In THF, this *B*-bromo compound **10c** reacts rapidly with the solvent to form *B*-(4-bromobutoxy)dicyclohexylborane (**11c**).[11]

The corresponding chloro and iodo compounds decompose more slowly, requiring 1–2 days. Again, the corresponding compounds **10** and **11** were observed by NMR, and **9** was found after AcOH protonolysis.

Typically an alkyl transfer from boron to carbon involves formation of an "ate" complex[12] as in the Zweifel trans-alkene synthesis (eq 5).[10] Thus, the rearrangement of **7**



reported here is unusual since it occurs without the addition of an equivalent of base. The possibility that this reaction is catalyzed by the presence of Lewis bases, such as halide ion or THF, seems unlikely since the reaction rate is similar in $CDCl_3$ and THF. If one is to make efficient use of compounds, such as **7**, the reactions must occur at a rate faster than that of the rearrangement. Therefore, reactions involving these compounds should be fast enough to be complete in 5–10 min at room temperature.

Experimental Section

General Comments. Standard techniques for handling air- and moisture-sensitive compounds were used.[13] Glassware was assembled hot or flamed out, while flushing with prepurified nitrogen. Reactions were carried out under a slight static pressure of nitrogen. The $CDCl_3$ was distilled from P_2O_5 and stored over 4-Å molecular sieves in the dark. THF was distilled from LAH. 9-BBN was prepared as previously described,[13] and solutions in THF were standardized by measurement of the H_2 evolved upon hydrolysis with MeOH/THF.[13] Chx_2BH was prepared from BH_3·SMe_2 immediately before use by a modification of the previously described procedure.[14] The 1-halo-1-alkynes were prepared by standard literature procedures.[15]

GC analyses were carried out on a HP5750 equipped with a Carbowax 20M column (10% on 60/80 Chromosorb W, 12 ft × 0.25 in). NMR data were obtained on a Varian FT-80A (^{13}C, 20.0 MHz; ^{11}B, 25.517 MHz) or a Varian XL-200 (^{13}C, 50.3 MHz). NMR samples were 10–20% by volume in the appropriate solvent ($CDCl_3$ or THF).

1-Alkenyldialkylboranes (3 and 4). Compounds **3** and **4** were synthesized as previously described.[2]

(1-Halo-1-alkenyl)dialkylboranes (7 and 8). The (1-halo-1-alkenyl)dialkylboranes were synthesized as reported[1] and isolated by removing the reaction solvent under vacuum (0.2 Torr). The appropriate solvent was then added for determination of the NMR spectra. For the Chx_2BH compounds, these operations were done quickly, and the samples kept at 0 °C until run to avoid problems from decomposition. Compounds **8g** and **8h** are low-melting solids. The others are moderately viscous liquids at room temperature, and all fume strongly when exposed to air.

Stability of (1-Bromo-1-hexenyl)dicyclohexylboranes (7c). Chx_2BH (10 mmol) was prepared in a flask having a septum-covered sidearm. THF (18.2 mL) and *n*-docecane (0.3712 g, 0.5 mL, GC internal standard) were added via syringe. 1-Bromo-1-hexyne (1.61 g, 1.3 mL, 10 mmol) was added dropwise while stirring the mixture in a room-temperature water bath. The total volume was then 20 mL. The mixture was stirred at room temperature, and samples (~0.2 mL) were removed occasionally with a double-ended needle and quenched with an excess of AcOH. The samples were treated by shaking with ~0.5 mL of 3 M K_2CO_3 and then drying with a small amount of K_2CO_3. GC analyses for **2c** and **9a** were then carried out. The results are shown in Figure 2.

Identification of the Products of Rearrangement of (1-Halo-1-alkenyl)dicyclohexylboranes (7) in THF and in $CDCl_3$. In a reaction similar to the previous one but without the internal standard, removal of the THF after rearrangement gave **11c** as a viscous liquid: ^{13}C NMR (Table I); ^1H NMR ($CDCl_3$) δ 5.45 (t, J = 7 Hz, H-2), 3.88 (t, J = 7 Hz, H-17), 3.42 (t, J = 7 Hz, H-20), 2.4–1.9 (br peak). The structure was assigned by comparison with ^{13}C and ^1H NMR spectra of similar known compounds. **12a** was synthesized by a known procedure,[10] and it shows a triplet in the ^1H NMR spectra at δ 5.48 ($CDCl_3$). The ^{13}C NMR spectra (Table I) also indicate the same carbon skeleton as **11c**. *B*-(4-Bromobutoxy)-9-BBN was made from the reaction of *B*-bromo-9-BBN with THF: ^1H NMR ($CDCl_3$) δ 3.98 (t, H-17), 3.42 (t, H-20), 2.2–1.2 (br peak); ^{13}C NMR ($CDCl_3$, same numbering scheme as compounds in Chart I) δ 32.99 (C-14), 22.96 (C-15), 64.59 (C-17), 33.09, 30.27, 29.11 (C-18, -19, and -20). Thus, a combination of data from the spectra of the 9-BBN compound having a *B*-(4-bromobutoxy) group and the spectra of **12a** accounts

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very well for the ^1H and ^{13}C NMR spectral features of **11c**. Also, protonolysis of **11c** gives **9a**, identified by comparison (^1H and ^{13}C NMR and GC) with an authentic sample prepared by protonolysis of **12a**. Rearrangement of **7c** in $CDCl_3$ gives **10c**, identified by its fast reaction with THF to give **11c**.

Studies of the decomposition of the other compounds **7** were carried out by allowing samples in $CDCl_3$ or $THF/CDCl_3$, in septum-covered NMR tubes to remain at room temperature for 1–2 days or at 50 °C for 3–6 h, respectively. Examination of the ^{13}C NMR spectra (Table I) indicated that the same rearrangement as observed with **7c** had occurred. The rearrangements were not always clean, especially in $CDCl_3$, and for **10g** a complex mixture was observed by ^{13}C NMR.

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Registry No. **2b**, 50586-18-0; **2c**, 13154-12-6; **2d**, 16538-47-9; **2f**, 64531-23-3; **2g**, 42843-49-2; **2h**, 52356-93-1; **3a**, 56962-83-5; **3e**, 62072-20-2; **4a**, 69322-45-8; **4e**, 73062-42-7; **5a**, 87393-77-9; **6a**, 79919-22-5; **6e**, 87393-78-0; **7b**, 87393-79-1; **7c**, 87393-80-4; **7d**, 87393-81-5; **7f**, 87393-82-6; **7g**, 87393-83-7; **7h**, 87393-84-8; **8b**, 87411-94-7; **8c**, 67826-84-0; **8d**, 87393-85-9; **8f**, 87393-86-0; **8g**, 87393-87-1; **8h**, 87393-88-2; **9a**, 16538-48-0; **9e**, 87393-89-3; **10b**, 87393-90-6; **10c**, 87393-91-7; **10d**, 87393-92-8; **10f**, 87393-93-9; **10g**, 87393-94-0; **10h**, 87393-95-1; **11b**, 87393-96-2; **11c**, 87393-97-3; **11d**, 87393-98-4; **11f**, 87393-99-5; **11g**, 87394-00-1; **11h**, 87394-01-2; **12a**, 87394-02-3; **12e**, 87394-03-4; Chx_2BH, 1568-65-6; 9-BBN, 280-64-8; *B*-(4-bromobutoxy)-9-BBN, 87394-04-5; *B*-bromo-9-BBN, 22086-45-9; 1-bromo-1-hexyne, 1119-64-8.

On the Relationship between Molecular Geometry and Excited-State Properties of 9-Anthrylalkenes†

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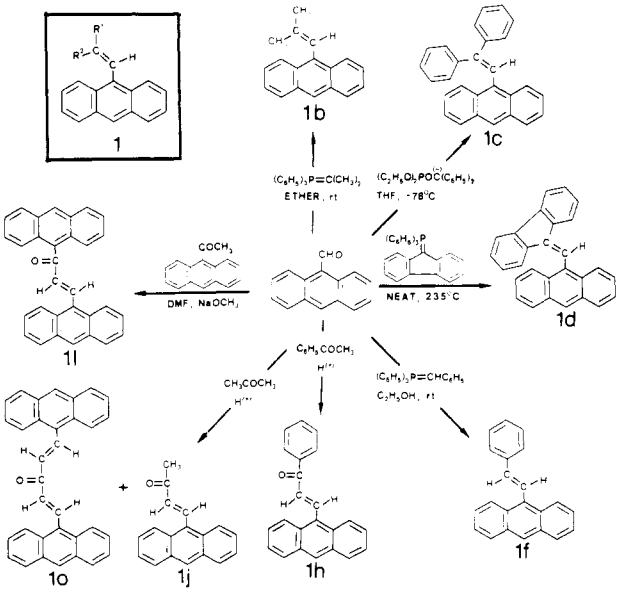
The excited-state properties of a series of 1-substituted and 1,1-disubstituted 2-(9-anthryl)alkenes have been investigated in terms of their fluorescence spectra and photochemical isomerizations. Large Stokes shifts of up to 10 000 cm^{-1} between absorption and emission maxima are attributed to geometrical differences between the ground state and the emitting excited state. The [cis]:[trans] ratio of the photostationary state was found to depend markedly on the nature of the 1-substituent. Photochemical isomerization of 1,3- and 1,5-bis(9-anthryl)-substituted trans olefins results in the formation of intramolecular [4π + 4π] or [4π + 2π] cycloaddition products. The cycloaddition reactions of carbonyl-substituted anthracenes are suggested to involve the triplet excited state.

The fluorescence spectrum of *trans*-1,2-bis(9-anthryl)-ethylene in solution at room temperature is characterized by a Stokes shift of about 10 000 cm^{-1}, indicating the large difference between the molecular ground-state geometry and the geometry of the emitting singlet excited state.[1,2] By contrast, *cis*-1,2-bis(9-anthryl)ethylene in solution at room temperature is nonfluorescent, most likely because its molecular geometry, which is characterized by two overlapping anthracene π systems in close proximity, enhances radiationless decay.[3] Geometrical factors probably also contribute to the photochemical isomerization of the cis isomer by intramolecular Diels–Alder reaction, which involves one anthracene moiety as a diene and the other as a dienophile.[4]

We have now investigated the relationship between molecular geometry and excited-state properties of a series of 9-anthrylethylenes of general structure **1** (cf. Scheme I). In ethylenes **1a–e**, R^1 and R^2 are identical, and, consequently, no net chemical change will be achieved by way of photochemical cis–trans isomerization. However, the photophysical properties of **1a–e**, such as electronic absorption and emission spectra, may be affected as the steric demand of R^2 increases. Compounds **1f–k** are three pairs of geometrical isomers in which R^1/R^2, being phenyl, benzoyl, and acetyl, may govern the multiplicity of the reacting excited state. Finally, in ethylenes **1l–q**, R^1/R^2 incorporates an additional 9-anthryl moiety, such as 9-anthrylcarbonyl or 9-anthrylmethyl, so that these compounds represent bichromophoric systems. In addition to cis–trans isomerization, intramolecular photochemical reactions involving the anthracene moieties are conceivable for **1–q**.

Scheme I



† Dedicated to Professor G. O. Schenck on the occasion of his 70th birthday.

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