Representative of the runs utilizing *N*-methylmaleimide, a solution of 5 g of imide **2**, 5 g of *N*-methylmaleimide, and 25 g of dimethyl phthalate was vaporized into the furnace at 750 °C, 2.5 mm pressure, and a contact time of ca. 10 ms. Effluent[17] from the traps was poured slowly into 600 mL of ether, giving several crops of crystalline solid upon standing. These were combined and recrystallized twice from tetrahydrofuran to give the Diels–Alder adduct **10** as flocculent, cream-colored crystals: mp 202–203 °C; IR (KBr) 1695 and 1760 cm^{-1} (s and w, imide C=O); ^1H NMR (DMF-d_6) δ 3.4–3.7 (m, CH, 2), overlapping resonances at 2.90 and 2.87 (2 s, CH_3), and 2.7–3.1 (m, CH_2) (total of 10 H); mass spectrum *m/e* (rel intensity) 248 (40, M^+), 244 (26), 200 (15), 191 (23), 163 (36), 106 (100), 105 (65). Anal. Calcd for $C_{12}H_{12}N_2O_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 58.09; H 4.90; N, 12.05.

Pyrolysis of Dinitrile 3. In a typical run, a solution of 25 g of dinitrile **3** and 25 g of benzonitrile was vaporized into the pyrolysis apparatus at 775 °C, 10 mm pressure, and a contact time of ca. 21 ms. The effluent (ca. 29 g) from a series of traps at −70 °C was taken up in 30 mL of tetrahydrofuran. Chilling at −20 °C gave 4.4 g of diene **12**, which, from ether, gave almost white needles of the pure (by VPC on a 5 ft × 0.25 in. Apiezon on Chromosorb T column) diene, mp 126–127 °C (by placing the capillary in the apparatus preheated to ca. 125 °C) (lit.[4] mp 125–127 °C). Dilution of the tetrahydrofuran mother liquor with ether gave an additional 1.44 g of the diene **12**: IR (KBr) 2220 (CN), 1570 (C=C), 950 cm^{-1} (=CH_2, overtone at 1900); ^1H NMR ($CDCl_3$) δ 6.45 and 6.33 (2 s, J_{gem} = 0 Hz); mass spectrum *m/e* (rel intensity) 104 (26, M^+), 77 (95), 64 (48), 52 (100). Anal. Calcd for $C_6H_4N_2$: C, 69.22; H, 3.87; N, 26.91. Found: C, 69.2; H, 4.0; N, 27.1.

Registry No.—1, 4336-19-0; **2**, 28839-49-8; **3**, 52477-67-5; **4**, 38818-30-3; **9**, 59082-62-1; **10**, 59120-88-6; **11**, 26011-79-0; **12**, 19652-57-4; cyclohexene-1,2-dicarboxylic anhydride, 4720-86-9; cyclohexene-1,2-dicarboxamide, 62601-01-8.

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(12) R. L. Cobb and J. E. Mahan, to be published.
(13) Melting points, determined in a Mel-Temp apparatus, are uncorrected; IR spectra were determined on a Perkin-Elmer Model 137 Infracord; NMR spectra were determined vs. internal Me_4Si on Varian T60 or XL100 instruments.
(14) M. E. Bailey and E. D. Amstutz, *J. Am. Chem. Soc.*, **78**, 3828 (1956).
(15) Recrystallization of the first product crop, 269 g, from ether gave a small amount of insoluble *N*-methylcyclohexene-1,2-dicarboxamic acid: mp 178–179 °C (from isopropyl alcohol–ether); IR (KBr) 3280 (sharp, strong, NH), 1630, 1540, and 1290 (amide), 1670 and 930 cm^{-1} (acid). Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 59.11; H, 7.19; N, 7.13.
(16) (a) G. E. Ficken and R. P. Linstead, *J. Chem. Soc.*, 4846 (1952); (b) G. E. Ficken, H. France, and R. P. Linstead, *ibid.*, 3730 (1954).
(17) VPC analyses for **9** and **10** were made utilizing the Carbowax column described in footnote *b* of Table I and a similar silicone rubber column.

Organoboranes. 21. Facile Syntheses of *cis*-Bicyclo[3.3.0]oct-1-yl Derivatives from Lithium Dialkyl-9-borabicyclo[3.3.1]nonane "Ate" Complexes[1]

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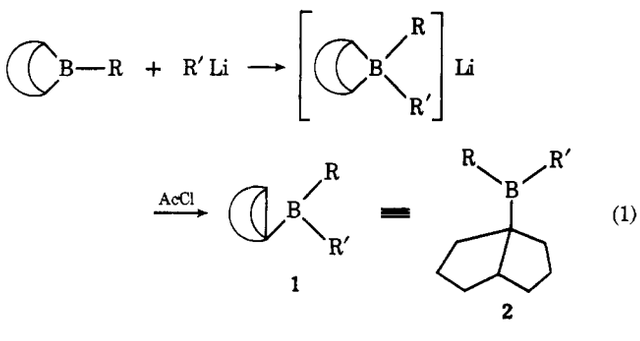
Received March 1, 1977

Lithium dialkyl-9-borabicyclo[3.3.1]nonane "ate" complexes react with acetyl chloride via hydride transfer to form *cis*-bicyclo[3.3.0]oct-1-yldialkylboranes. These organoboranes are valuable intermediates for the preparation of a variety of 1-substituted *cis*-bicyclo[3.3.0]octanes. Many of these derivatives have heretofore been difficult to prepare. However, the ready availability of the organoborane precursor now permits their convenient preparation in high yield.

We recently reported that lithium "ate" complexes (**1**), derived from the addition of alkyllithiums to *B*-alkyl-9-borabicyclo[3.3.1]nonanes (*B*-alkyl-9-BBN), react with acetyl chloride via hydride transfer to form *cis*-bicyclo[3.3.0]oct-1-yldialkylboranes (**2**) (eq 1).[2,3] These organoboranes are valuable intermediates for the preparation of a variety of 1-substituted *cis*-bicyclo[3.3.0]octanes. Since many of these derivatives have heretofore been difficult to prepare, we explored the synthetic utility of these organoboranes (**2**).[4] Employing several common reaction sequences from the organoborane arsenal, we prepared and isolated in high yield several representative 1-substituted *cis*-bicyclo[3.3.0]octanes (**3**–**7**).



(1)

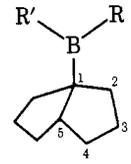
The preparations of compounds **5**–**7** deserve further discussion. These synthetic procedures are known to proceed via free-radical reaction paths.[6–9] Accordingly, we felt that the proper choice of the other alkyl groups (R and R′ in **2**) would be important to the overall success in effecting preferential transfer of the bicyclic moiety. To demonstrate this point, we carried out 1,4-additions to methyl vinyl ketone with several derivatives of **2** with varying alkyl substituents. The results (Table I) clearly show, as anticipated, that selective migration

Table I. Reaction of *cis*-Bicyclo[3.3.0]oct-1-yldialkylboranes with Methyl Vinyl Ketone

Registry no.	2	R	R'	5,[a] %	$RCH_2CH_2COCH_3$,[a] %	$R'CH_2CH_2COCH_3$,[a] %
59322-84-8	2a	Methyl	Methyl	90	Tr	
62726-59-4	2b	Methyl	Ethyl	86	*b*	13
62726-60-7	2c	Methyl	Isopropyl	47	*b*	42
62726-61-8	2d	Methyl	*tert*-Butyl	32	*b*	66
62726-62-9	2e	Methyl	*n*-Butyl	98	*b*	4
59322-87-1	2f	*n*-Butyl	*n*-Butyl	96	7	

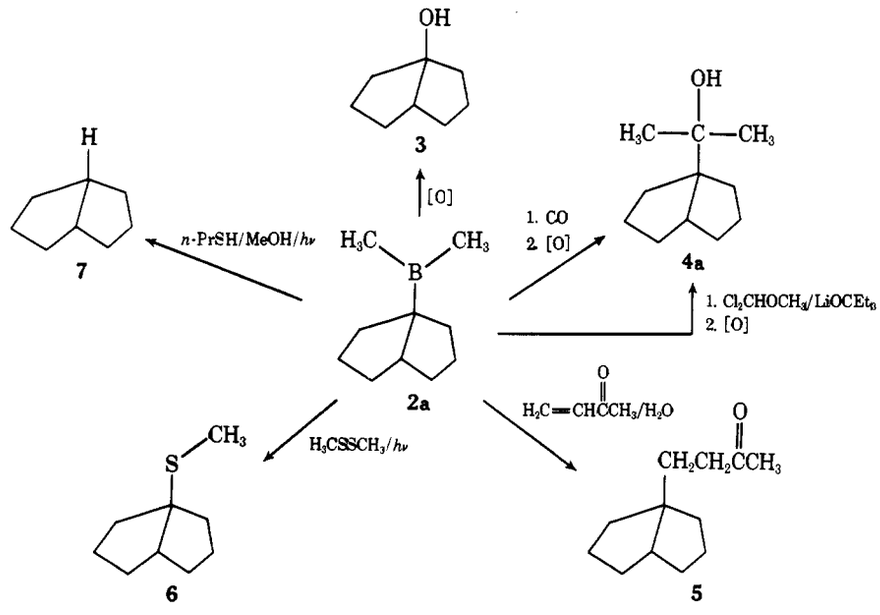
[a] GLC yields. [b] Amount of methyl transfer product not determined.

Table II. ^{13}C and ^{11}B NMR of Some *cis*-Bicyclo[3.3.0]oct-1-yldialkylboranes



Compd		^{13}C NMR chemical shift of carbon						^{11}B NMR chemical shift
	R	R'	1[a]	2	3	4	5	Other	
2a	Methyl	Methyl		36.9	26.4	35.0	45.9	~12[b]	−81.9
2b	Methyl	Ethyl		36.8	26.3	35.0	45.7	~19,[b] 8.7[d]	−82.7
2c	Methyl	Isopropyl		36.5	26.3	35.1	45.5	~5,[b] 17.9[d]	−81.3
2d	Methyl	*tert*-Butyl		36.8	26.3	35.0	46.7	~9,[b] 28.0[d]	−80.3
2e	Methyl	*n*-Butyl		37.0	26.0	35.3	45.8	~8.5,[b] 27.2,[c] 13.8,[d] 26.5, 27.6	−82.7
2f	*n*-Butyl	*n*-Butyl		36.7	26.3	35.3	45.5	24.8,[c] 13.8,[d] 24.6, 27.0	−81.8

[a] Bridgehead carbon α to boron not detected. [b] α-Methyl carbon. [c] α-Methylene. [d] Terminal methyl carbon.



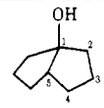
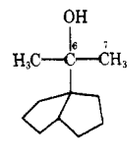
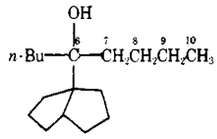
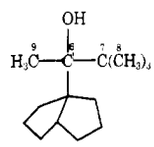
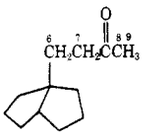
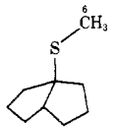
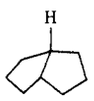
of the bicyclic moiety is enhanced when the other groups are methyls or other primary groups, but decreases seriously with the presence of a secondary or tertiary alkyl substituent. The use of the dimethyl derivative (**2a**) offers the further advantage that the boron-containing by-products of these reactions are volatile and easily removed with the solvent.[10-12]

In our preparations of these bicyclic derivatives (**2–7**), we observed only evidence for the *cis*-bicyclo[3.3.0]octane products. If trans isomers formed, they were present in concentrations below the detectability of ^{13}C NMR (Tables II and III). This may seem surprising in view of the free-radical nature of some of the syntheses. However, examination of molecular models reveals that the *trans*-bicyclo[3.3.0]octyl ring system is greatly strained as compared with the cis-fused isomer. Consequently, it is probable that the bicyclic radical produced in these reactions is constrained into the pyramidal conformation. The complete retention of stereochemistry in these reactions is therefore not unreasonable.

Experimental Section

General Comments. The techniques described in Chapter 9 of ref 6 were used extensively. All glassware was dried at 140 °C for at least 4 h, assembled hot, and allowed to cool under a purge of prepurified nitrogen. The reaction flasks were fitted with side arms capped with rubber septa and were flamed out under a nitrogen purge immediately before use. All reactions were carried out under a static pressure of prepurified nitrogen. The transfer of liquids and solutions of or-

Table III. ^{13}C NMR of Some *cis*-Bicyclo[3.3.0]oct-1-yl Derivatives[a]

Registry no.	Compd	Chemical shift of carbon 1	2	3	4	5	Other
52318-93-1	3 	90.9	42.2	26.1	33.7	52.0	
62726-63-0	4a 	62.1	38.0	26.2	34.9	45.0	^{6}75.0 ^{7}26.7
62726-64-1	4b 	63.7	38.2	26.3	35.1	45.5	^{6}77.9 23.9 27.1 36.9 ^{10}14.1
62726-65-2	4d 	65.9	40.7	28.4	36.1	49.0	^{6}80.5 ^{7}36.3 ^{8}29.1 ^{9}23.1
62726-66-3	5 	53.2	39.2	25.9	34.3	49.9	^{6}35.6 ^{7}40.9 ^{8}209.0 ^{9}29.9
62726-67-4	6 	60.9	41.1	26.0	34.1	50.9	^{6}12.9
1755-05-1	7 	43.4	34.3	26.4	34.3	43.4	

[a] Spectra recorded of GLC purified samples in $CDCl_3$.

ganometallics were done either with oven-dried, nitrogen-purged hypodermic syringes fitted with stainless steel needles or by the double-ended needle technique.[6] All reactions were stirred magnetically using over-dried, Teflon-coated stirring bars. Photoinduction of reactions was accomplished by placing a Sears 275-W sunlamp about 3 in. from the reaction flask. The rubber septa on the reaction flasks were covered with aluminum foil and positioned away from the lamp to prevent their decomposition. All distillations were carried out using a short path assembly without a column.

Materials. THF and diethyl ether were distilled from lithium aluminum hydride prior to use, degassed with nitrogen, and stored in large ampules with Teflon stopcocks. Technical grade pentane (and hexane) was stirred for 1 day over concentrated sulfuric acid, treated with anhydrous potassium carbonate, distilled from lithium aluminum hydride, degassed with nitrogen, and stored in crown-capped bottles. Acetyl chloride was freshly distilled from calcium hydride. Methanol (Mallinckrodt SpectAR) was dried over 3 Å molecular sieves. The dichloromethyl methyl ether (Aldrich) was freshly distilled prior to use. Lithium triethylcarboxide was prepared by the addition of neat triethylcarbinol (Chemical Samples Co.) to a hexane solution of *n*-butyllithium. Methyl vinyl ketone (Aldrich) was distilled immediately before use to remove any polymerization inhibitor. Dimethyl disulfide and 1-thiopropane (Aldrich) were used as received. The 9-BBN (mp 149–151 °C) and the *B*-alkyl-9-BBN derivatives were prepared as previously described.[13] Methyllithium (from methyl chloride) in diethyl ether (Orgmet) and other organolithium reagents (Alfa) were carefully standardized prior to use by the method of Watson and Eastham.[14] The concentration of the hydrogen peroxide solution was determined by refractive index.[15]

Analyses. ^{11}B NMR spectra were recorded on a Varian XL-100-15 spectrometer (32.1 MHz) using a Nicolet 1080 data system. The spectra were recorded in the CW mode using ^{2}H internal or ^{19}F external locks; all chemical shifts are relative to $BF_3{\cdot}OEt_2$ (δ 0) with the chemical shifts downfield from $BF_3{\cdot}OEt_2$ assigned as negative. ^{1}H NMR spectra were recorded on a Varian T-60 (60 MHz) spectrometer, while the ^{13}C NMR spectra were taken on a Varian CFT-20 (20 MHz, FT) instrument. Both the ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane (δ 0). Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer. The samples were thin films of neat material held between salt plates.

GLC analyses were carried out on a Hewlett-Packard 5752B chromatograph fitted with a Disc integrator using 6 ft × 0.25 in. stainless steel columns filled with 10% loaded packing on AW-DMCS treated 60/80 Chromosorb W. SE-30 was used for the analyses of the organoboranes, while either XE-60 or XF-1150 were used for the analyses of the non-boron-containing materials. Preparative GLC was carried out on a modified Wilkins A-100 chromatograph using 5 ft × 0.5 in. columns filled with 20% loaded packing on AW-DMCS treated 60/80 Chromosorb W. Either SE-30 or XE-60 liquid phases were employed.

***cis*-Bicyclo[3.3.0]oct-1-yldimethylborane (2a). General Procedure.** To an oven-dried, nitrogen-flushed, 250-mL flask fitted with a magnetic stirring bar, septum inlet, and reflux condenser connected to a mercury bubbler were added 21.77 g (160.1) mmol of *B*-methyl-9-BBN[13,6] and 50 mL of dry, olefin-free pentane. Stirring was begun, and the flask was cooled to −78 °C where 90.5 mL of 1.77 M (160.1 mmol) methyllithium in diethyl ether was added slowly via double-ended needle. After stirring about 10 min at −78 °C, the slurry was allowed to come to room temperature and stir for 2 h. The flask was then immersed in an ice–water bath while 11.4 mL (160.1 mmol) of freshly distilled acetyl chloride was added dropwise from a syringe. A vigorous reaction ensued, and a white precipitate formed. After stirring about 2 h at room temperature, the supernatant liquid was decanted via double-ended needle into an evacuated short-path distillation assembly where the volatiles were flash distilled. The precipitate was washed with pentane (3 × 20 mL) and the washings decanted in like manner into the distillation apparatus. The residual oil was vacuum distilled giving 22.3 g (93% yield) of a clear, colorless

Table IV. 1-Substituted *cis*-Bicyclo[3.3.0]octanes

Compd	Yield, %	Rxn scale, mmol	GLC[a] purity, %	Bp, °C (Torr)	n_D^{20}	IR[c] ν, cm^{-1}				^1H NMR ($CDCl_3$),[c] δ ppm
3	75	79.9	91	95–97 (20)	~30[b] (42–43)[b,c]	3375 (s)	1200 (s)	1050 (m)	870 (m)	2.1 (m, 1 H)
						1450 (s)	1170 (m)	1005 (s)	820 (w)	0.9–2.0 (m, 12 H)
						1315 (s)	1125 (m)	980 (s)		~1.2 (s, 1 H)[d]
						1295 (m)	1075 (m)	930 (m)		
4a R = methyl R′ = methyl	62	4.7	99[c]			3490 (s)	1380 (s)	1070 (m)	810 (m)	2.4 (m, 1 H)
						1470 (s)	1240 (m)	950 (m)		1.1–2.2 (m, 13 H)
						1460 (s)	1150 (s)	930 (s)		1.15 (s, ~6 H)
						1390 (s)	1120 (s)	870 (m)		
4b R = *n*-butyl R′ = *n*-butyl	87	20.8	94	97–99 (0.02)	1.4860	3500 (m)	1375 (m)	1015 (m)	740 (m)	2.4 (m, 1 H)
						1460 (s)	1330 (m)	990 (m)		1.1–2.2 (m, 25 H)
						1450 (s)	1120 (m)	920 (m)		0.93 (dist t, ~6 H)
4d R = methyl R′ = *tert*-butyl	41	3.8	99[c]		41[b,c]	3540 (s)	1365 (s)	1110 (s)	920 (m)	2.75 (m, 1 H)
						1470 (s)	1300 (s)	1070 (s)	895 (s)	1.1–2.3 (m, 13 H)
						1400 (s)	1210 (s)	1010 (s)	820 (m)	1.25 (s, ~3 H)
						1380 (s)	1150 (m)	965 (m)		1.05 (s, 9 H)
5	90	42.7	94	72–75 (0.02)	1.4736 (1.4773)[c]	1720 (vs)	1405 (m)	1360 (s)	1160 (s)	2.3–2.6 (m, 3 H)
						1450 (s)	1380 (s)			2.17 (s, 3 H)
										1.1–2.2 (m, ~14 H)
6	91	31.7	87	114–116 (40)	1.5009 (1.5106)[c]	1460 (s)	1290 (m)	1070 (m)	920 (m)	2.05 (s, 3 H)
						1440 (vs)	1220 (m)	1000 (m)	910 (m)	1.2–2.0 (m, ~13 H)
						1430 (s)	1190 (s)	960 (m)	890 (m)	
						1310 (m)	1120 (m)	950 (m)	810 (m)	
7	75	30.3	96	75–78 (95)	1.4609 (1.4620)[c]	2920 (vs)	1480 (m)	1340 (w)	920 (m)	2.4 (m, 2 H)
						2860 (s)	1460 (s)	1240 (w)		1.0–2.0 (m, 12 H)

[a] GLC purity after simple vacuum distillation. [b] Melting point. [c] After further purification by preparative GLC. [d] Concentration dependent chemical shift, exchanges with D_2O.

oil, **2a**, bp 73–76 °C (18 Torr). GLC examination of the distillate showed it to be greater than 94% pure.

***cis*-Bicyclo[3.3.0]octan-1-ol (3). *In Situ* Procedure.** To an oven-dried, nitrogen-flushed, 500-mL flask fitted as described above, there were added 9.75 g (79.9 mmol) of solid 9-BBN and 50 mL of dry, olefin-free pentane. Stirring was begun, and 4.5 g (160 mmol, 100% excess) of ethylene was bubbled into the slurry over 2 h. After stirring for 5 h, the mixture was cooled to −78 °C, and 45.2 mL of 1.77 *M* (80.0 mmol) methyllithium (from methyl chloride) in diethyl ether was added slowly via double-ended needle. After stirring for 10 min at −78 °C, the slurry was allowed to warm to room temperature and stir for 2 h, at which point the solid completely dissolved. The mixture was cooled with an ice–water bath while 5.70 mL (80.1 mmol) of acetyl chloride (freshly distilled from calcium hydride) was added slowly from a syringe. The reaction mixture was allowed to warm to room temperature and stir for 2 h, and then recooled to 0 °C, where it was oxidized using 28 mL of 3.0 *M* sodium hydroxide and 28 mL of 30% hydrogen peroxide.[16] To ensure completion of the oxidation, the mixture was maintained at 50 °C for 1 h. After the addition of 56 g of potassium carbonate, the organic layer was separated and the aqueous phase extracted with diethyl ether (3 × 30 mL). The combined extracts were transferred to a distillation assembly where the volatiles were removed in vacuo and the residual oil vacuum distilled. There was collected 7.5 g (75% yield) of a waxy solid, **3** [mp ~30 °C, bp 95–97 °C (20 Torr)].

***cis*-Bicyclo[3.3.0]oct-1-yldi-*n*-butylcarbinol (4b). Carbonylation Method.** A 110-mL high-pressure bomb was thoroughly flushed with nitrogen and then charged with 4.87 g (20.8 mmol) of **2f**, 40 mL of THF, and 1.7 mL (30 mmol, 50% excess) of ethylene glycol. The bomb was pressurized with carbon monoxide (60 atm) and then heated to 150 °C for 16 h. After cooling and depressurization, the contents of the bomb were transferred to a 100-mL flask. The mixture was oxidized using 7.0 mL of 6 *M* sodium hydroxide, 7.0 mL of ethanol, and 7.0 mL of 30% hydrogen peroxide.[16] After heating to 50 °C for 2 h to ensure complete oxidation, the mixture was saturated with sodium chloride and the organic layer separated. The aqueous phase was extracted with pentane (2 × 15 mL). The combined extracts were decanted into an evacuated distillation assembly where the volatiles were flash distilled. The residual oil was vacuum distilled, and 4.55 g (87% yield) of a colorless oil (**4b**) was collected, bp 97–99 °C (20 Torr).

***cis*-Bicyclo[3.3.0]oct-1-yl)butan-2-one (5).** To a nitrogen-flushed, 100-mL flask fitted with a magnetic stirring bar and septum inlet were added 6.4 g (42.7 mmol) of **2a**, 20 mL of THF, 1.5 mL (85 mmol, 100% excess) of water, and 5.20 mL (64.0 mmol, 50% excess) of freshly distilled methyl vinyl ketone. Stirring was begun, and 10 mL of air was bubbled through the solution. The mixture was allowed to stir for 24 h. The volatiles were removed in vacuo and the residual liquid vacuum distilled to give 6.9 g (90% yield) of product (**5**), bp 72–75 °C (20 mTorr).

***cis*-Bicyclo[3.3.0]oct-1-yl Methyl Sulfide (6).** To an oven-dried, nitrogen-flushed, 100-mL flask fitted with a septum inlet, magnetic stirring bar, and reflux condenser connected to a mercury bubbler were added 4.75 g (31.7 mmol) of **2a**, 25 mL of hexane, and 2.85 mL (31.7 mmol) of dimethyl disulfide. The mixture was irradiated with a Sears 275-W sunlamp. The solvent was allowed to boil. After 2 h, the volatiles were removed in vacuo and the residual oil vacuum distilled to give 4.5 g (91% yield) of a colorless liquid (**6**), bp 114–116 °C (40 Torr).

***cis*-Bicyclo[3.3.0]octane (7).** To an oven-dried, nitrogen-flushed, 50-mL flask fitted with a septum inlet, magnetic stirring bar, and reflux condenser connected to a mercury bubbler were added 4.54 g (30.3 mmol) of **2a**, 2.0 mL of methanol, and 1.0 mL of 1-thiopropane. The mixture was irradiated with a Sears 275-W sunlamp for 1 h. The volatiles were removed in vacuo and the residual liquid vacuum distilled giving 2.5 g (75% yield) of product (**7**), bp 75–78 °C (95 Torr).

Acknowledgment. The authors express appreciation to the National Science Foundation for the support of this work under Grants GP41169X and CHE 76-20846.

Registry No.—*B*-methyl-9-BBN, 23418-81-7; *B*-butyl-9-BBN, 23532-74-3; methyllithium, 917-54-4; ethyllithium, 811-49-4; isopropyllithium, 1888-75-1; *tert*-butyllithium, 594-19-4; butyllithium, 109-72-8; 9-BBN, 280-64-8; dimethyl disulfide, 624-92-0; methyl vinyl ketone, 78-94-4.

References and Notes

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Hydroboration. 48. Effect of Structure on Selective Monohydroboration of Representative Nonconjugated Dienes by 9-Borabicyclo[3.3.1]nonane

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Received April 26, 1977

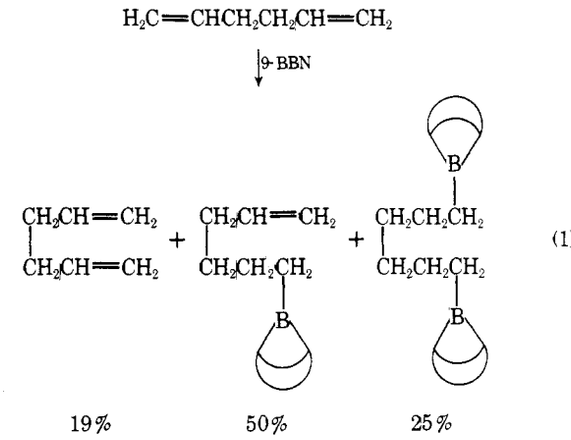
The exceptionally high sensitivity toward structure exhibited by 9-borabicyclo[3.3.1]nonane (9-BBN) in the hydroboration of simple olefins carries over to the hydroboration of nonconjugated dienes. In this way many such dienes can be selectively monohydroborated and thereby converted into synthetically useful intermediates. For example, dienes containing one terminal double bond and one internal double bond can be selectively hydroborated at the terminal position. Whereas 2-methyl-1,4-pentadiene is selectively hydroborated by disiamylborane at the less substituted double bond, the greater reactivity of 9-BBN for the 2-methyl-1-alkene structure permits the preferential hydroboration of the other position. The hydroboration of certain symmetrical cyclic dienes, such as 1,4-cyclohexadiene and 1,5-cyclooctadiene, with 9-BBN (1:1 mole ratio) is readily controlled to produce the monoadducts. The observation that the relative reactivities of simple olefin structures toward hydroboration with 9-BBN can be carried over so reliably to predict the point of hydroboration of nonconjugated dienes greatly facilitates the utilization of such dienes as intermediates in organic synthesis.

9-Borabicyclo[3.3.1]nonane is an interesting hydroborating agent which exhibits unusual regio-[2] and stereospecificities.[3] It also exhibits a remarkable sensitivity to the structure of individual olefins.[4] The question arose as to whether this knowledge could be carried over to predict the course of the monohydroboration of representative dienes. If so, such dienes could be selectively monohydroborated and the products utilized in the many transformations now available for organoboranes.[5] Accordingly, we undertook to study the monohydroboration of a number of representative nonconjugated dienes with this reagent and to compare the results with those realized in an earlier study utilizing disiamylborane.[6]

Results and Discussion

The reaction procedure involved the addition of a standard solution of 9-BBN in tetrahydrofuran (THF) to an equivalent amount of the diene in the same solvent. An internal standard suitable for GC analysis was present. The reaction was allowed to proceed to completion at 25 °C. The reaction product was oxidized by alkaline hydrogen peroxide in the usual manner.[5] GC examination for residual diene established the extent of monohydroboration (0% diene = 100% monohydroboration; 50% diene = 0% monohydroboration). The mono-ol product revealed the point or points of attack.

Symmetrical Acyclic Dienes. The reaction of 9-BBN with symmetrical dienes, such as 1,4-pentadiene and 1,5-hexadiene, would be expected to proceed in an essentially statistical manner, giving 25% residual diene, 50% of the monohydroboration products, and 25% of the dihydroboration product. Indeed, the data for 1,6-hexadiene closely follow this prediction for statistical behavior, with a minor discrepancy in the residual 1,5-hexadiene (eq 1).



(1)

The results for 1,4-pentadiene are similar, but reveal a moderate displacement from the purely statistical distribution (eq 2). Conceivably there could be a small interaction of the double bond with the boron atom in the monohydroboration product sufficiently significant as to retard slightly its conversion into the dihydroboration product.

Similar results are realized with disiamylborane.[6]

Symmetrical Cyclic and Bicyclic Dienes. In contrast to the behavior of the symmetrical acyclic dienes, the hydroboration of certain symmetrical cyclic dienes with 9-BBN can be controlled to yield the monohydroboration product predominantly. In the case of 1,5-cyclooctadiene, the results differ