

Hydroboration. XXXV. Cyclic Hydroboration of 2,4-Dimethyl-1,4-pentadiene and 2,5-Dimethyl-1,5-hexadiene. A Simple Synthesis of Bis(3,5-dimethyl)borinane and Bis(3,6-dimethyl)borepane and Their Application to the 1,4-Addition Reaction of Organoboranes¹

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Abstract: The hydroboration of 2,4-dimethyl-1,4-pentadiene (2,4-DMP) or 2,5-dimethyl-1,5-hexadiene (2,5-DMH) with borane in THF at 0° in the molar ratio of 1:1 with the diene-to-borane mode of addition is rapid and complete immediately following the addition of diene. The oxidation product derived from 2,4-DMP consists of a 98:2 mixture of 2,4-dimethyl-1,5-pentanediol and its isomer, while that from 2,5-DMH is a 90:10 mixture of the 1,6-diol and its isomer. Little or no position isomerization occurs at 25°, but at 70° a slow isomerization is evident in the product from 2,5-DMH. The initial hydroboration mixture contains only ca. 50% of either bis(3,5-dimethyl)borinane (3,5-DMBN) or bis(3,6-dimethyl)borepane (3,6-DMBP). The presence of fully alkylated polymeric species, presumably the 3:2 dumbbell-shaped products, and unreacted borane in THF is indicated. The amount of 3,5-DMBN or 3,6-DMBP increases with time, requiring approximately 24 hr at 25° or 1 hr at 70° to attain the maximum yields of 90–94% (3,5-DMBN) or 75% (3,6-DMBP). Consequently, the hydroboration of 2,4-DMP or 2,5-DMH with borane in THF in the molar ratio of 1:1 followed by a brief heating of the reaction mixture at reflux provides a simple synthesis of 3,5-DMBN or 3,6-DMBP. 3,5-DMBN has been isolated and identified. 3,6-DMBP has not been isolated, but has been fully identified. The dimeric nature of these compounds has been established by the typical bridge absorption in the ir at 1650–1565 cm⁻¹. Treatment of these compounds with alcohols produces the corresponding *B*-alkoxy derivatives. The hydroboration of olefins with a solution in THF containing a modest excess of 3,5-DMBN or 3,6-DMBP proceeds smoothly, requiring approximately 1 hr with 1-hexene, 1-octene, isobutylene, 2-butene, cyclopentene, and norbornene, 2 hr with 2-methyl-2-butene, 4–8 hr with cyclohexene, and 16–24 hr with 2,3-dimethyl-2-butene. The hydroboration products containing *B*-alkyl-3,5-DMBN or *B*-alkyl-3,6-DMBP can in most cases be used for further operations following quenching of residual hydride. Distillation provides *B*-alkyl-3,5-DMBN (98–99% pure) or *B*-alkyl-3,6-DMBP (~90% pure) in excellent yields. Alternatively, the reaction of *B*-methoxy-3,5-DMBN with alkyllithium produces the corresponding *B*-alkyl-3,5-DMBP in excellent yields. These *B*-alkylboracyclanes undergo a facile reaction with methyl vinyl ketone and similar α,β -unsaturated carbonyl derivatives to transfer the *B*-alkyl group from boron to carbon, especially readily when the *B*-alkyl group is secondary or tertiary. This extension of the 1,4-addition reaction *via* organoboranes to highly branched secondary and tertiary alkyl groups makes this reaction broadly applicable to the formation of carbon-carbon bonds utilizing alkyl and cycloalkyl groups with a wide range of structures.

Recently we have largely clarified the course of the reaction of representative straight-chain dienes,³ such as 1,3-butadiene,^{3b-e} 1,4-pentadiene,^{3b,f} and 1,5-hexadiene,^{3b,g} with borane (BH₃) in tetrahydrofuran (THF). In summary, the hydroboration of these dienes capable of producing common rings is highly cyclic, forming the corresponding dumbbell-shaped molecules with two cyclic moieties as the initial major products. The formation of higher polymers observed in the case of 1,3-butadiene and 1,4-pentadiene under certain reaction conditions is largely a result of the remarkably facile opening of the boracyclopentane ring system.^{3e,f,4}

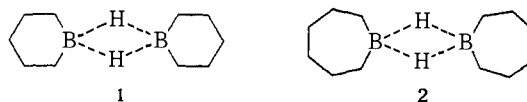
(1) For preliminary reports on some aspects of the present study, see H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, **93**, 3777 (1971); *J. Organometal. Chem.*, **28**, C1 (1971).

(2) Postdoctoral Research Associate on a Research Grant, DA 31-134 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

(3) (a) H. C. Brown and E. Negishi, *Pure Appl. Chem.*, **29**, 527 (1972); (b) G. Zweifel, K. Nagase, and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 183 (1962); (c) E. Breuer and H. C. Brown, *ibid.*, **91**, 4164 (1969); (d) H. C. Brown, E. Negishi, and S. K. Gupta, *ibid.*, **92**, 2460 (1970); (e) E. Negishi, P. L. Burke, and H. C. Brown, *ibid.*, **93**, 3400 (1971); (f) E. Negishi, P. L. Burke, and H. C. Brown, *ibid.*, **94**, 7431 (1972); (g) P. L. Burke, E. Negishi, and H. C. Brown, *ibid.*, **95**, 3654 (1973).

(4) H. C. Brown, E. Negishi, and P. L. Burke, *ibid.*, **92**, 6649 (1970).

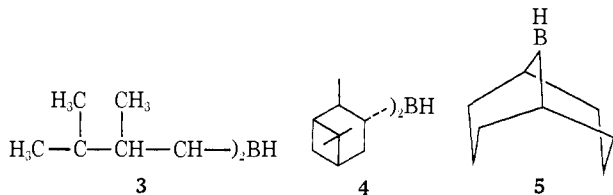
As a consequence of the highly cyclic nature of the hydroboration reaction, the directive effect observed in the case of 1,4-pentadiene and 1,5-hexadiene is considerably different from that predicted by extrapolating the results realized with terminal monoolefins. For example, the ratio of 1,5- and 1,4-pentanediols obtained in the hydroboration of 1,4-pentadiene with borane followed by oxidation is approximately 40:60.^{3b,f} This should be compared with the predicted statistical ratio of 89:11 calculated from the ratio of 94:6 for the 1 and 2 isomers realized from simple 1-alkenes.⁵ Thus, various attempts to realize a simple hydroboration of 1,4-pentadiene or 1,5-hexadiene to form bisborinane (1) or bisborepane (2) as a pure product have been unsuccessful.^{3f,g,6}



(5) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(6) For the synthesis of 1 and 2 by indirect procedures, see H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **26**, C67 (1971), and references 3f and g.

In recent years, various dialkylboranes, such as disiamylborane⁵ (3), diisopinocampheylborane⁵ (4), and 9-borabicyclo[3.3.1]nonane (9-BBN)⁷ (5), have been

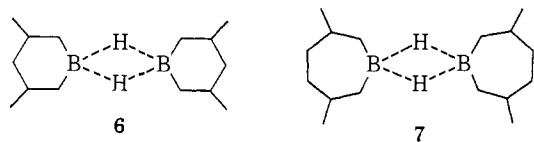


developed as useful reagents. All of these dialkylboranes have two secondary alkyl groups attached to the boron atom. New developments in the area of free-radical reactions of organoboranes have made it desirable to have available stable dialkylboranes with two primary alkyl groups attached to a boron atom.⁸

Therefore, it was of both theoretical and practical interest to us to establish whether the abnormal directive effect resulting from cyclic hydroboration can be circumvented by utilizing the greater directive effect of the C(CH₃)=CH₂ moiety in hydroboration.⁵ If

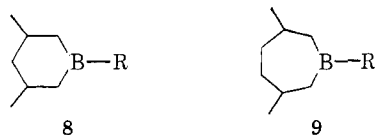


so, the hydroboration of 2,4-dimethyl-1,4-pentadiene and 2,5-dimethyl-1,5-hexadiene with borane in THF in the molar ratio of 1:1 might proceed in a simple manner to produce 3,5-dimethylborinane (6) and 3,6-dimethylborepane (7), respectively. Moreover, based



on our preliminary results with bisborinane (1), these cyclic dialkylboranes, with the boron atom attached to two primary carbon atoms, could be expected to be especially useful for application as reagents for the free-radical reactions of organoboranes.

In order to test these possibilities, we undertook to clarify the course of the reaction of 2,4-dimethyl-1,4-pentadiene and 2,5-dimethyl-1,5-hexadiene with borane in THF and to establish the reaction condition required to produce 6⁹ and 7 cleanly and quantitatively. We also hoped to study the hydroboration of olefins with 6 and 7 to form the corresponding *B*-alkyl-3,5-dimethylborinanes (8) and *B*-alkyl-3,6-dimethylborepanes (9). Finally, we sought to explore the appli-



cability of 8 and 9 to representative free-radical reactions of organoboranes.

(7) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280, 5281, 5283 (1968).

(8) H. C. Brown and M. M. Midland, *Angew. Chem., Int. Ed. Engl.*, **11**, 692 (1972).

(9) This compound has been previously obtained from 2,4-dimethyl-1,3-pentadiene by an indirect method: R. Köster, *Advan. Organometal. Chem.*, **2**, 257 (1964).

Results and Discussion

Hydroboration of 2,4-Dimethyl-1,4-pentadiene with Borane in Tetrahydrofuran. The hydroboration of 2,4-dimethyl-1,4-pentadiene (2,4-DMP) with borane in THF in the molar ratio of 1:1 was carried out at 0° utilizing the diene-to-borane mode of addition. The hydroboration reaction was complete immediately following the addition of 2,4-DMP, as indicated by analysis for active hydride. After the mixture was stirred for 1 hr at 0°, oxidation of an aliquot produced 2,4-dimethyl-1,5-pentanediol¹⁰ and an apparently isomeric diol¹¹ in the ratio of 98:2 in 99% overall yield. In the case of the parent compound, 1,4-pentadiene, the ratio of 1,5- and 1,4-pentanediols is 42:58.^{3f} The directive effect of the C(CH₃)=CH₂ moiety⁵ must be responsible for the large difference in isomer distribution in these two related cases. No significant change was observed over 24 hr at 25° in either the overall yield or the isomeric distribution of the diols.

Examination by glpc of a methanolized aliquot at 1 hr indicated the formation of bis(3,5-dimethyl)borinane (3,5-DMBN) (6) in a yield of 50%. This result, coupled with the presence of a band of considerable intensity at 2400 cm⁻¹ for borane in THF, suggests an extensive formation of fully alkylated, more complex species along with the 3,5-DMBN. No attempts were made to clarify the nature of these higher alkylated species. However, based on our previous studies³ it is probable that they consist largely of the 3:2 dumbbell-shaped compound (10). The amount of 3,5-DMBN increased with time (90% in 24 hr), while the amount of active hydride remained essentially constant at near the theoretical value. The experimental results are summarized in Table I. Based on these

Table I. Hydroboration of 2,4-Dimethyl-1,4-pentadiene with Borane in THF in the Molar Ratio of 1:1 with the Diene-to-Borane Mode of Addition (100-mmol Scale)

Time, ^a hr	Residual hydride, mmol	<i>B</i> -Methoxyboracyclane, ^b mmol		2,4-Dimethylpentanediol, ^c mmol			
		I ^c	II ^d	Total	1,5-	1,4-	Total
1 at 0°	100	50	3	53			
3	96	76	1	77	97	2	99
6	96	85	Trace	85			
24	100	89	Trace	89	95	2	97
24 then 1 at 70°	100	94	Trace	94	97	3	100

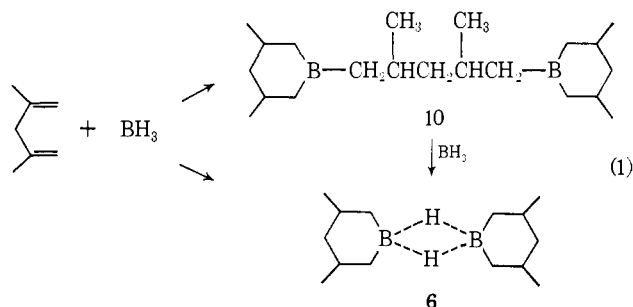
^a Time of stirring at 25° after completion of addition, unless otherwise stated. ^b Glpc analysis (SE-30). ^c I = *B*-methoxy-3,5-dimethylborinane. ^d II = not identified. Presumably, *B*-methoxy-2,2,4-trimethylborolane. ^e Glpc analysis of the oxidation product after silylation with Tri-Sil.

results we may tentatively depict the course of the reaction as shown in eq 1.

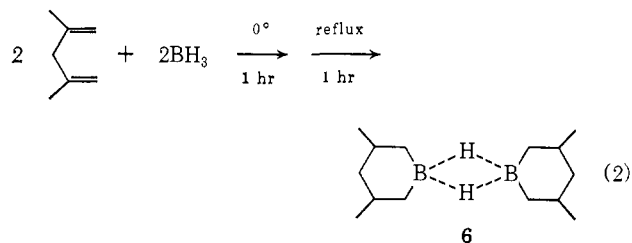
In order to accelerate the formation of 3,5-DMBN the hydroboration mixture (after 1 hr) was refluxed at 70°. The amount of 3,5-DMBN reached 94% of the theoretical in 1 hr. Neither detectable loss of active hydride nor change in the diol distribution was observed (Table I). Thus, the hydroboration of 2,4-

(10) Presumably a mixture of the diastereomers, arising from the oxidation of the *cis*- and *trans*-3,5-dimethylborinane moiety. Our attempts to separate these isomeric species by glpc have been unsuccessful. However, see footnote 13.

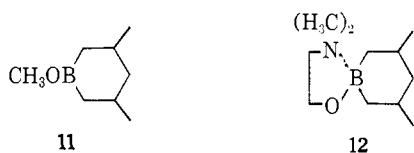
(11) Not identified but presumably 2,4-dimethyl-1,4-pentanediol.



DMP with borane in THF in the molar ratio of 1:1 (0°, 1 hr), followed by refluxing the reaction mixture for 1 hr, achieves a simple synthesis of 3,5-DMBN in THF (eq 2), which can be used directly for most further



purposes as described later. After evaporation of the solvent, distillation provided 3,5-DMBN, bp 79–82° (1 mm), in 87% yield. The compound was fully identified by (1) the analyses of the oxidation products (2,4-dimethyl-1,5-pentanediol and boric acid), (2) active hydride analysis, (3) ir (1565 (s) cm⁻¹), and (4) nmr. Presence of the strong band at 1565 cm⁻¹ and essential absence of any bands in the 2400–2600-cm⁻¹ region establishes the dimeric nature of 3,5-DMBN.¹² On methanolysis at 25° the compound was readily converted into *B*-methoxy-3,5-dimethylborinane¹⁰ (11) in 98% yield, with evolution of the theoretical amount of hydrogen. Similarly, treatment of 6 with *N,N*-dimethylaminoethanol produced in 83% yields a relatively stable derivative 12 which yielded the correct analyses and expected spectral data.



Hydroboration of 2,5-Dimethyl-1,5-hexadiene with Borane in Tetrahydrofuran. The hydroboration of 2,5-dimethyl-1,5-hexadiene (2,5-DMH) with borane in THF was carried out in a manner similar to that described for 2,4-dimethyl-1,4-pentadiene. The experimental results are summarized in Table II.

The experimental results parallel closely those obtained with 2,4-dimethyl-1,4-pentadiene. Thus, the hydroboration reaction is rapid but the amount of bis(3,6-dimethyl)borepane (3,6-DMBP) (7) reaches its maximum only after 12 hr at 25°. These results support the following dual path scheme (eq 3) similar to that shown in eq 1.

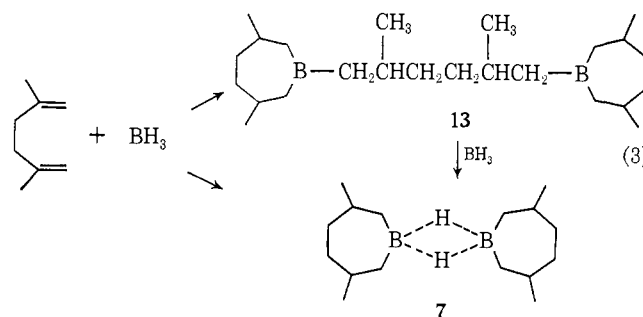
As shown in Table II, the amount of 3,6-DMBP did not exceed 75% at any time within 24 hr. As in the case of 3,5-DMBN, refluxing the hydroboration mix-

(12) (a) W. J. Lehmann and I. Shapiro, *Spectrochim. Acta*, **17**, 396 (1961); (b) E. Negishi, J. J. Katz, and H. C. Brown, *J. Amer. Chem. Soc.*, **94**, 4025 (1972).

Table II. Hydroboration of 2,5-Dimethyl-1,5-hexadiene with Borane in THF in the Molar Ratio of 1:1 with the Diene-to-Borane Mode of Addition (100-mmol Scale)

Time, ^a hr	Residual hydride, mmol	Methanolysis —products, ^b mmol—			2,5-Dimethyl- hexanediol, ^d mmol		
		<i>B</i> -Me- thoxy- 3,6- DMB	I ^c	Total	Diol	Other diols	Total
0	100	46	4	50			
1	98	50	5	55	85	8	93
3	103	54	5	59			
6	98	65	6	71			
12	96	75	6	81			
24	98	74	6	80	88	7	95

^{a,b} See the corresponding footnotes of Table I. ^c I = unidentified compound. Presumably *B*-methoxy-2,2,5-trimethylborinane. ^d See footnote e of Table I.



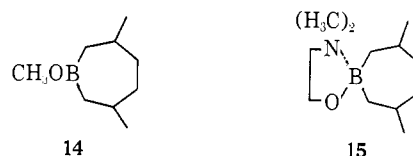
ture accelerated the formation of 3,6-DMBP. The experimental results of the thermal treatment are summarized in Table III.

Table III. Thermal Treatment at *Ca.* 70° of the Hydroboration Mixture Obtained by the Reaction of 2,5-Dimethyl-1,5-hexadiene with Borane in THF in the Molar Ratio of 1:1 (100-mmol Scale)

Time, ^a hr	Residual hydride, mmol	Methanolysis —product, ^b mmol—			2,5-Dimethyl- hexanediol, ^d mmol		
		<i>B</i> -Me- thoxy- 3,6- DMBP	I ^c	Total	Diol	Other diols	Total
0	100	46	5	51	86	11	97
1	98	74	7	81	85	14	99
3	94	73	8	81	84	14	98
6	94	75	7	82	86	15	101
24	95	73	8	81	82	14	96
48	92	70	15	85	75	20	96

^a Time of refluxing at *ca.* 70°. ^{b-d} See the corresponding footnotes in Table II.

Unlike the case of 3,5-DMBN, an attempt to isolate 3,6-DMBP by distillation even at low pressure resulted in its partial decomposition. However, its identity was established by its conversion to *B*-methoxy-3,6-dimethylborepane (14) in 84% yield, which was further converted quantitatively to a more stable derivative 15.

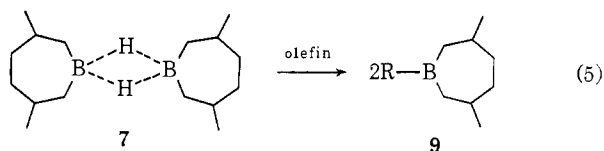


The dimeric nature of 3,6-DMBP was established by ir spectroscopy (1560 (s) cm⁻¹). Only a very weak band

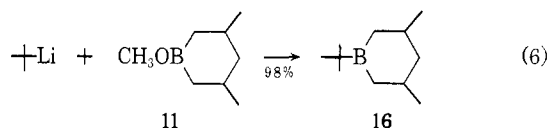
at 2510 cm^{-1} was observed in the 2400–2600- cm^{-1} region.¹²

Syntheses of *B*-Alkyl-3,5-dimethylborinanes and *B*-Alkyl-3,6-dimethylborepanes. The hydroboration of many representative olefins, such as 1-hexene, 1-octene, isobutylene, 2-butene, 2-methyl-2-butene, cyclopentene, and norbornene, with a modest excess (25–50% in active hydride) of a THF solution containing 3,5-DMBN or 3,6-DMBP was quite rapid, being essentially over within 1–2 hr at 25°. After the usual oxidation, the corresponding alcohols were obtained in 95–100% yields (by glpc). The isomeric purity of 1-hexanol, 1-octanol, isobutyl alcohol, and 3-methyl-2-butanol obtained in this manner was ~99%, indicating that both 3,5-DMBN and 3,6-DMBP provide considerable control over the direction of hydroboration. With less reactive olefins, such as cyclohexene and 2,3-dimethyl-2-butene, the hydroboration was slower, requiring 4–8 hr with cyclohexene and 16–24 hr with 2,3-dimethyl-2-butene (Table VI).

The hydroboration of olefins with 3,5-DMBN or 3,6-DMBP is essentially free of disproportionation, yielding the corresponding *B*-alkylboracyclanes¹³ in excellent yields (eq 4 and 5).



It is also possible to synthesize certain *B*-alkylboracyclanes, such as *B*-(*tert*-butyl)-3,5-dimethylborinane (16), which are not accessible by the hydroboration route, by the reaction of the *B*-methoxyboracyclanes (11 and 14) with appropriate alkyl lithium compounds¹⁴ (eq 6). No sign of isomerization of the *tert*-butyl group to an isobutyl group was observed.¹⁵



The experimental results are summarized in Table IV.

Reaction of *B*-Alkyl-3,5-dimethylborinanes and *B*-Alkyl-3,6-dimethylborepanes with α,β -Unsaturated Carbonyl Derivatives. The free-radical reaction of trialkylboranes with α,β -unsaturated carbonyl derivatives¹⁶ is one of the most general and useful reactions which organoboranes undergo. A serious limitation in applying this highly promising reaction to organic synthesis has been the requirement for the fully substituted boranes, R_3B . It is difficult to obtain these

(13) Glpc examination of these *B*-alkylboracyclanes in most cases revealed the presence of two partially resolved peaks of comparable sizes in addition to a minor peak, indicating that they exist as the *cis* and *trans* mixtures.

(14) We are indebted to G. Kramer for the establishment of this procedure.

(15) G. F. Hennion, P. A. McCusker, and A. J. Rutkowski, *J. Amer. Chem. Soc.*, **80**, 617 (1958).

(16) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, G. W. Kabalka, and G. W. Holland, *ibid.*, **92**, 3503 (1970), and references cited therein.

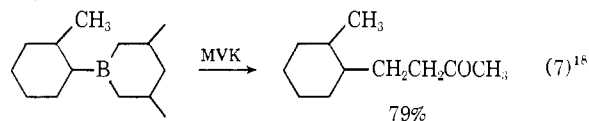
Table IV. Syntheses of *B*-Alkyl-3,5-dimethylborinanes and *B*-Alkyl-3,6-dimethylborepanes

<i>B</i> -Alkylboracyclane ^a	Yield, %		Bp, °C (mm)
	Glpc	Iso-lated	
<i>B</i> -(<i>n</i> -Hexyl)-3,5-dimethylborinane ^b	95	90	122–124 (17)
<i>B</i> -Cyclopentyl-3,5-dimethylborinane ^b	93	84	112–114 (17)
<i>B</i> -(<i>tert</i> -Butyl)-3,5-dimethylborinane	98	88	72–73 (11)
<i>B</i> -(<i>n</i> -Hexyl)-3,6-dimethylborepane ^c	97	89	108–112 (3)
<i>B</i> -Cyclopentyl-3,6-dimethylborepane ^c	98	91	96–100 (3)

^a Identified by glpc analyses of the oxidation products. Satisfactory pmr and ir spectra were also obtained. ^b The product contains 1–2% of a ring-contracted isomer. ^c The product contains ~10% of a ring-contracted isomer.

boranes when R is a bulky group. Thus, highly substituted olefins, such as 1-methylcyclohexene and 2,3-dimethyl-2-butene, do not undergo hydroboration to the R_3B stage.⁵ All attempts to synthesize tri-*tert*-butylborane have failed.¹⁵ Although 9-BBN (5) hydroborates these olefins to form the corresponding *B*-alkyl-9-BBN,⁷ their reaction with α,β -unsaturated carbonyl derivatives is complicated by the competitive participation of the ring moiety. For example, the reaction of *B*-cyclopentyl-9-BBN with methyl vinyl ketone (MVK) provided only a 24% yield of 4-cyclopentyl-2-butanone, although all of the starting borane disappeared. In our search for a better reagent, we have found that bisborinane (borinane) (1) satisfies most of the requirements. Thus, the reaction of *B*-cyclohexylborinane with MVK readily produced 4-cyclohexyl-2-butanone in 80% yield. The success with bisborinane suggested to us to apply 3,5-DMBN (6) and 3,6-DMBP (7), which are more readily obtainable than bisborinane, to the 1,4-addition reaction. We also reasoned that the presence of the appropriately situated two methyl groups would destabilize a free radical formed by the homolytic ring opening, thereby promoting a more selective participation of the *B*-alkyl group in the reaction.

Highly successful results were obtained with a wide variety of *B*-alkyl-3,5-DMBN and *B*-alkyl-3,6-DMBP derivatives. Thus, the reaction of *B*-cyclohexyl-3,5-DMBN with MVK using the standard conditions reported earlier¹⁷ provided the desired 4-cyclohexyl-2-butanone in a yield of 81%. More important, no difficulty was encountered in applying the new procedure to the homologation of more hindered groups, such as 2-methylcyclohexyl, *tert*-butyl, and 2,3-dimethyl-2-butyl (eq 7–9).



We selected MVK as a test system. However, other α,β -unsaturated carbonyl derivatives, such as 3-pentenone and 2-cyclohexenone, proved to be equally applicable.

The experimental results are summarized in Table V. The results with *B*-alkylborinanes are also tabulated for comparison.

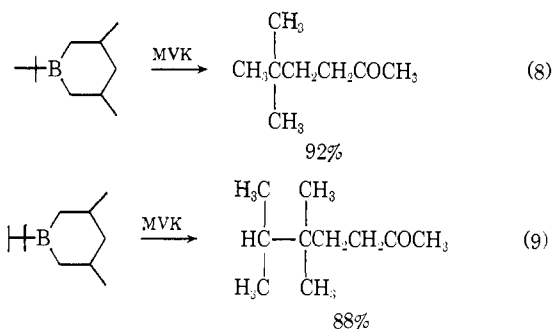
(17) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **89**, 5708 (1967).

(18) A mixture of *trans* and *cis* isomers in the ratio of 82:18 was obtained. The structural assignment is based on the pmr data and the refractive indices (n_D^{20} (*trans*) 1.4568 and n_D^{20} (*cis*) 1.4628).

Table V. Reaction of *B*-Alkylboracyclanes with α,β -Unsaturated Carbonyl Derivatives

Alkyl group of <i>B</i> -alkylboracyclane	α,β -Unsaturated carbonyl derivative ^a	Product ^b	Yield, %		
			3,5- DMBN ^d	3,6- DMBP ^e	Borinane ^f
<i>sec</i> -Butyl	MVK	5-Methyl-2-heptanone	83 (75) ^g	80	74 (67) ^g
Cyclopentyl	MVK	4-Cyclopentyl-2-butanone	78	65	66
Cyclohexyl	MVK	4-Cyclohexyl-2-butanone	81	74	80
Cyclohexyl	EA	4-Cyclohexyl-2-pentanone	71		
<i>trans</i> -2-Methylcyclohexyl	MVK	4-(2'-Methylcyclohexyl)-2-butanone ^h	79 (73) ^g		
<i>exo</i> -Norbornyl	MVK	4-Norbornyl-2-butanone ⁱ	81	61	65
<i>tert</i> -Butyl	MVK	5,5-Dimethyl-2-hexanone	90 (76) ^g		
<i>tert</i> -Butyl	CH	3-(<i>tert</i> -Butyl)cyclohexanone	73		
2,3-Dimethyl-2-butyl	MVK	5,5,6-Trimethyl-2-heptanone	88 (81) ^g	51	75 (71) ^g
<i>n</i> -Hexyl	MVK	2-Decanone ^{j, k}	32	51	

^a MVK, methyl vinyl ketone; EA, ethylideneacetone; CH, 2-cyclohexenone. ^b All products were either compared with authentic samples or exhibited spectral data in accordance with the assigned structures. All new products yielded the correct elemental analyses. ^c By glpc. Based on the olefin or alkyllithium used. ^d Using *B*-alkyl-3,5-DMBN. ^e Using *B*-alkyl-3,6-DMBP. ^f Using *B*-alkylborinane. ^g Numbers in parentheses are isolated yields. ^h See ref 18. ⁱ A single compound by glpc. Presumably the *exo* isomer. ^j Contaminated with 3% of an isomeric product.



Isolation of the desired products offered no difficulty. Simple distillation of the reaction mixture was usually sufficient. In cases in which the by-products, such as *B*-hydroxyboracyclanes, interfered with the distillation, the difficulty could be avoided by the alkaline hydrogen peroxide oxidation of the reaction mixture prior to distillation.

It is evident that the present development extends the 1,4-addition reaction to hindered secondary and tertiary alkyl groups, simultaneously providing a substantial improvement in the yields of the desired products based on the starting olefins or alkyllithium compounds. In view of the increasing number of reactions of organoboranes being uncovered which involve free-radical mechanisms, it appears probable that application of the presently described *B*-alkylboracyclanes to these reactions will also prove advantageous.

Experimental Section

The organoboranes were always handled under nitrogen with careful exclusion of oxygen and moisture. Pmr and ir spectra were obtained with Varian T-60 and Perkin-Elmer 137 B, respectively.

Materials. The preparation of borane solutions in THF was carried out as described previously.¹⁹ 2,4-Dimethyl-1,4-pentadiene (n^{20}_D 1.4179) and 2,5-dimethyl-1,5-hexadiene (n^{20}_D 1.4290) were obtained from Chem. Samples Co. and used as supplied. Glpc examination indicated they were at least 99% pure. Commercially available 1-hexene, 1-octene, isobutylene, 2-butene, cyclopentene, cyclohexene, norbornene, 2-methyl-2-butene, 1-methylcyclohexene, 2,3-dimethyl-2-butene, methanol, *tert*-butyllithium, and straight-chain hydrocarbons (internal standards) were used without additional purification.

Hydroboration of 2,4-Dimethyl-1,4-pentadiene with Borane in THF in the 1:1 Molar Ratio with the Diene-to-Borane Mode of Addition. In a 200-ml flask equipped with a magnetic stirrer, a

thermometer-well, a septum-inlet, and a condenser the tip of which was connected to a mercury bubbler were placed 27.8 ml (100 mmol) of 3.61 *M* borane in THF, 4.52 g (20 mmol) of *n*-hexadecane, and 50 ml of THF. To this was added at *ca.* 0° over 15 min 9.6 g (100 mmol) of 2,4-dimethyl-1,4-pentadiene. The total volume was measured to be 98 ml. One hour later the temperature was allowed to rise to 25°. The mixture was stirred at this temperature for 24 hr and then refluxed at *ca.* 70° for 1 hr. At appropriate times, a 5-ml aliquot was quenched with 0.5 ml of absolute methanol (evolution of gas was quite rapid at 25° and was normally complete in 5–10 min) and the methanolyzed aliquot analyzed by glpc using a 2-ft SE-30 column. The active hydride analysis was also performed by hydrolyzing a 1-ml aliquot. At 3 and 24 hr the methanolyzed aliquot was oxidized with 2.5 ml each of 3 *N* sodium hydroxide and 30% hydrogen peroxide and the products were analyzed by glpc, using a 6-ft SE-30 column, after the usual work-up and silylation with Tri-Sil. At 1 hr the ir spectrum indicated the presence of a strong band at 1565 cm^{-1} and a medium band at 2400 cm^{-1} . A minor band at 2600 cm^{-1} was also observable. Although all of the three bands were still observable at 24 hr, those at 2400 and 2600 cm^{-1} were very weak. The results are summarized in Table I.

Hydroboration of 2,5-Dimethyl-1,5-hexadiene with Borane in THF in the Molar Ratio of 1:1 with the Diene-to-Borane Mode of Addition. The same apparatus as used in the previous experiment was used. 2,5-Dimethyl-1,5-hexadiene (11.0 g, 100 mmol) was added dropwise over 15–20 min to 43.5 ml of 2.3 *M* borane in THF (100 mmol) at 20–25° (*n*-hexadecane as an internal standard). At appropriate times, 6-ml aliquots (10 mmol) were withdrawn and quenched with 1 ml of methanol. The amount of active hydride was measured, and the resulting mixture was analyzed by glpc (SE-30, 2 ft). The remaining mixture was oxidized, worked up, and analyzed by glpc after silylation as described in the previous experiment. The results are summarized in Table II. Thermal treatment of the hydroboration mixture was carried out by refluxing it at *ca.* 70°. At appropriate times aliquots were withdrawn and analyzed as described above (Table III).

Preparation of Bis(3,5-dimethyl)borinane (3,5-DMBN) (6). (A) 3,5-DMB in THF. In the same set-up as described in the previous experiments were placed 27.8 ml (100 mmol) of 3.61 *M* borane in THF and 50 ml of THF. To this was added at 0° over 15 min 9.6 g (100 mmol) of 2,4-dimethyl-1,4-pentadiene. The temperature of the mixture was allowed to rise to 25° over 30 min, and the mixture was refluxed at *ca.* 70° for 1 hr. After cooling under nitrogen, the total volume was adjusted to 100 ml by the addition of 7 ml of THF. For most further reactions the resulting solution of 3,5-DMBN in THF was directly used after determining the concentration.

(B) Isolation of 3,5-DMBN. After evaporation of the solvent of the reaction mixture obtained above, distillation provided 9.6 g (87%) of 3,5-DMBN: bp 79–82° (1 mm); ir (neat) strong bands at 2980, 2930, 1565, 1460, 1420, 1380, 1360, 1330, 1250, 1230, 1170, 1090, 1060, 943, and 854 cm^{-1} ; pmr (CCl_4 , TMS) δ 0–1.2 (m, sharp peaks at 0.83, 0.97, and 1.02), 1.2–1.6 (8, centered at 1.36), and 1.6–2.4 (m) ppm.

A sample of 3,5-DMBN (1.10 g, 5 mmol) was methanolyzed with 1 ml (*ca.* 25 mmol) of methanol at 25°. At this temperature and at 743 mm, 255 ml of hydrogen was evolved within 15 min (99%).

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

Glpc examination after addition of 0.45 g of *n*-hexadecane indicated the presence of 9.8 mmol (98%) of *B*-methoxy-3,5-DMBN contaminated with a trace quantity (<1%) of an isomeric compound. The methanolized mixture was oxidized as usual with 5 ml each of 3 *N* sodium hydroxide and 30% hydrogen peroxide. After the usual work-up and silylation, glpc examination on a 6-ft SE-30 column indicated the presence of 10.0 mmol (100%) of 2,4-dimethyl-1,5-pentanediol and 0.2 mmol (2%) of an apparently isomeric compound. Another 5-mmol sample of 3,5-DMBN was oxidized in the same manner, and the oxidized mixture was used for boron analysis.

Anal. Calcd for $C_{14}H_{30}B_2$: B, 9.83. Found: B, 10.03.

Preparation of Bis(3,6-dimethyl)borepane (3,6-DMBP) (7) in THF. A solution containing 3,6-DMBP was prepared from 11.0 g (100 mmol) of 2,5-dimethyl-1,5-hexadiene and 43.5 ml of 2.3 *M* borane in THF in a manner analogous to that described in the previous experiment. An attempt to distill 3,6-DMBP at *ca.* 0.1 mm resulted in a partial decomposition of 3,6-DMBP as indicated by the observation of a wide boiling range.

Preparation of *B*-Methoxy-3,5-dimethylborinane (11). Bis(3,5-dimethyl)borinane (2.20 g, 10 mmol) was methanolized by the addition of 2 ml of absolute methanol at 25° and the methanolysis product distilled to give 2.4 g (85%) of *B*-methoxy-3,5-dimethylborinane (11): bp 59–60° (18 mm); pmr (CCl_4 , TMS) δ 0.3–1.2 (m, intense sharp peaks at 0.85 and 0.97, 10 H), 1.2–1.5 (t, centered at 1.33, 2 H), 1.6–2.4 (m, 2 H), and 3.62 (s, 3 H); ir (neat) 1370 (s) cm^{-1} .

Preparation of *B*-(2'-Dimethylamino)ethoxy-3,5-dimethylborinane (12). 2-Dimethylaminoethanol (1.03 g, 11.6 mmol) was added at 25° to 1.28 g (5.8 mmol) of bis(3,5-dimethyl)borinane in 5 ml of pentane. After gas evolution subsided, the mixture was distilled to give 1.9 g (83%) of 12: bp 110° (3 mm); n_D^{20} 1.4835; pmr (CCl_4 , TMS) δ -0.5–0.5 (m, 2 H), 0.7–1.0 (m, intense peaks at 0.82 and 0.93, 6 H), 1.1 (t, 2 H, *J* = 6 Hz), 1.4–2.2 (m, 2 H), 2.45 (s, 6 H), 2.83 (t, 2 H, *J* = 7 Hz), and 3.83 (t, 2 H, *J* = 7 Hz); ir (neat) characteristic strong bands at 1250, 1115, 1095, and 1070 cm^{-1} .

Anal. Calcd for $C_{11}H_{24}NBO$: C, 67.02; H, 12.27; N, 7.11; B, 5.49. Found: C, 67.28; H, 12.27; N, 7.18; B, 5.70.

Preparation of *B*-Methoxy-3,6-dimethylborepane (14). A 10-ml aliquot of a solution of 3,6-DMBP in THF (20 ml, 0.5 *M*) was methanolized by the addition of 20 ml of absolute methanol and the methanolysis product distilled to give 2.50 g (81%) of 14: bp 76–79° (20 mm); pmr (CCl_4 , TMS) δ 0.8–1.3 (10 H, m), 1.3–2.2 (6 H, m), and 3.57 (3 H, s) ppm; ir (neat) 1320 (s) cm^{-1} .

Preparation of *B*-(2'-Dimethylamino)ethoxy-3,6-dimethylborepane (15). *B*-Methoxy-3,6-dimethylborepane (1.54 g, 10 mmol) was treated at 25° with 0.94 g (10.5 mmol) of 2-dimethylaminoethanol. Distillation of the reaction mixture afforded 2.0 g (95%) of 15: bp 104–105° (1 mm); n_D^{20} 1.4825; pmr (CCl_4 , TMS) δ 0.4–1.1 (10 H, including two sharp peaks at 0.83 and 0.95), 1.1–2.0 (6 H, m), 2.4 (6 H, s), 2.6–3.0 (2 H, t), 3.6–4.0 (2 H); ir (neat) 1275 (m), 1100 (m), 1065 (m) cm^{-1} . *Anal.* Calcd for $C_{12}H_{26}NBO$: C, 68.25; H, 12.41; B, 5.12; N, 6.63. Found: C, 68.26; H, 12.33; B, 5.00; N, 6.43.

Preparation of 2,5-Dimethyl-1,6-hexanediol. Disiamylborane was prepared by the addition of 14.0 g (200 mmol) of 2-methyl-2-butene to 43.5 ml (100 mmol) of 2.3 *M* borane at 0–10°. One hour later, 2,5-dimethyl-1,5-hexadiene (5.5 g, 50 mmol) was added to the solution of disiamylborane at 0–10°. After the usual oxidation and work-up, distillation provided 2,5-dimethyl-1,6-hexanediol in 89% yield (6.5 g): bp 110° (1 mm); n_D^{20} 1.4574; ir (neat) 3450 (s), 1045 (s) cm^{-1} ; pmr ($CDCl_3$, TMS) δ 0.9 (d, 6 H), 1.1–2.0 (m, 6 H), 3.40 (d, 4 H), and 4.23 (broad s, 2 H) ppm. Glpc examination (SE-30) of the product after silylation with Tri-Sil revealed the presence of two peaks in the ratio of 98:2.

Hydroboration of Olefins with Bis(3,5-dimethyl)borinane or Bis(3,6-dimethyl)borepane. In a 100-ml flask with a septum-inlet, a magnetic stirring bar, and an outlet connected to a mercury bubbler was placed 30 ml of 0.8 (or 1.0) *M* 3,5-DMBN (or 3,6-DMBP) in THF. To this was added at 25° (water bath) 10 ml of a solution in THF containing 20 mmol of an olefin and 10 mmol of an internal standard. At appropriate times aliquots were withdrawn, quenched with methanol, and analyzed by glpc using a column packed with CW-20M, SE-30, or adiponitrile. 1-Hexene, 1-octene, isobutylene, 2-butene, cyclopentene, and norbornene were uptaken ($\geq 99\%$) within 1 hr. The hydroboration of 2-methyl-2-butene with either 3,5- or 3,6-DMB took 2 hr to complete. The approximate rate data with cyclohexene and 2,3-dimethyl-2-butene are summarized in Table VI.

Table VI. Hydroboration of Cyclohexene and 2,3-Dimethyl-2-butene with Bis(3,5-dimethyl)borinane or Bis(3,6-dimethyl)borepane at 25°

Olefin	Hydroborating agent	Olefin reacted, ^a %					
		1 hr	2 hr	4 hr	8 hr	16 hr	24 hr
Cyclohexene	3,5-DMBN	81	88	97	99		
	3,6-DMBP	62	70	88	99		
2,3-Dimethyl-2-butene	3,5-DMBN	75	84	88		98	

^a By glpc analysis of methanolized aliquots.

In each case the final hydroboration mixture was oxidized and analyzed by glpc (CW-20M). The yields of alcohols were 95–100%. The isomeric purity of 1-hexanol, 1-octanol, isobutyl alcohol, or 3-methyl-2-butanol was $\sim 99\%$. The stereochemistry of norbornanol was not established.

Preparation of *B*-Alkyl-3,5-dimethylborinanes and *B*-Alkyl-3,6-dimethylborepanes by the Hydroboration of Olefins with Bis(3,5-dimethyl)borinane and Bis(3,6-dimethyl)borepane. The following procedure for the preparation of *B*-cyclopentyl-3,5-dimethylborinane is representative. To 0.25 ml (25 mmol) of a 1 *M* solution of 3,5-DMBN in THF was added at 25° 2.72 g (40 mmol) of cyclopentene. One hour later 1 ml of methanol was added to destroy the residual hydride. Distillation of the mixture afforded 6.0 g (84%) of *B*-cyclopentyl-3,5-DMBN: bp 112–114° (17 mm); pmr (CCl_4 , TMS) δ 0.2–2.3 (complex pattern with major peaks at 0.83, 0.97, 1.0, and 1.57 ppm); ir (neat) 2950 (s), 1460 (s) cm^{-1} . Glpc examination (SE-30) of the distilled product revealed the presence of two peaks in the ratio of 99:1. Oxidation of the product yielded cyclopentanol (98% yield) and 2,4-dimethyl-1,5-pentanediol (95% yield).

Preparation of *B*-(*tert*-Butyl)-3,5-dimethylborinane. In a 100-ml flask with a septum-inlet, a magnetic stirrer, and an outlet connected to a mercury bubbler were placed 2.96 g (21.2 mmol) of *B*-methoxy-3,5-DMBN, 0.57 g (5 mmol) of *n*-octane, and 20 ml of pentane. At -78° 10.3 ml (21.2 mmol) of 2.06 *M tert*-butyllithium (2.11 *M* in total base) was added over 2–3 min. The cooling bath was removed 30 min later, at which time the reaction mixture was clear. The temperature was allowed to rise to 25° over 15 min, during which time the entire mixture became turbid and precipitates were formed. Two hours later the stirring was stopped, and the supernatant solution was analyzed by glpc (SE-30). There was present 20.8 mmol (98%) of *B*-(*tert*-butyl)-3,5-dimethylborinane.¹³ The reaction mixture was directly distilled to provide 3.0 g (88%) of *B*-(*tert*-butyl)-3,5-dimethylborinane: bp 72–73° (11 mm); pmr (CCl_4 , TMS) δ 0.2–1.8 (complex multiplet with an intense peak at 0.87, 21 H) and 1.8–2.3 (m, 2 H) ppm; ir (neat) 2950 (s), 1470 (s), 1320 (s) cm^{-1} . After oxidation of a sample of distilled *B*-(*tert*-butyl)-3,5-dimethylborinane glpc examination revealed the presence of *tert*-butyl alcohol (98%, 12-ft SE-30) and 2,4-dimethyl-1,5-pentanediol (10%, after silylation) contaminated with an isomeric diol by $\sim 1\%$.

Reaction of *B*-Alkylboracyclanes with α,β -Unsaturated Carbonyl Derivatives. The following procedure for the reaction of *B*-thexyl-3,5-DMBN with MVK to form 5,5,6-trimethyl-2-heptanone is representative. *B*-Thexyl-3,5-DMBN was prepared by the reaction of 3.36 g (40 mmol) of 2,3-dimethyl-2-butene with 25 ml (25 mmol) of a 1 *M* solution of 3,5-DMBN in THF for 18 hr at 25°. After destroying the residual hydride with 1.8 ml (100 mmol) of water, 4.2 g (60 mmol) of MVK and 2.26 g (10 mmol) of *n*-hexadecane (internal standard) were added and the reaction mixture was stirred overnight at 25°. Glpc examination indicated the presence of 35.2 mmol (88% based on 2,3-dimethyl-2-butene) of 5,5,6-trimethyl-2-heptanone. The reaction mixture was oxidized with 20 ml each of 3 *N* sodium hydroxide and 30% hydrogen peroxide in order to destroy *B*-hydroxy-3,5-DMBN. The aqueous layer was saturated with sodium chloride. The organic layer was separated and the aqueous layer was extracted with pentane. After drying over magnesium sulfate, the combined organic layer was distilled to yield 5.05 g (81%) of 5,5,6-trimethyl-2-heptanone: bp 95–97° (20 mm); n_D^{20} 1.4356; ir (neat) 1720 cm^{-1} ; pmr (CCl_4 , TMS) δ 0.8 and 0.9 (12 H), 1.2–1.7 (m, 3 H), 1.9–2.5 (m, 5 H). *Anal.* Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 77.02; H, 12.97.

Isolation and Identification of *trans*- and *cis*-4-(2'-Methylcyclo-

hexyl)-2-butanones. An 82:18 mixture of *trans*- and *cis*-4-(2'-methylcyclohexyl)-2-butanones was prepared in 73% yield (79% by glpc), bp 76–80° (1.6 mm). The two isomers were separated by glpc using a 10% Carbowax 20M column. The major component was the *trans* isomer: n^{20}_D 1.4568; pmr (CCl₄, TMS) δ 0.6–2.0 (complex multiplet with three major peaks at 0.93, 1.40, and 1.75 ppm, 15 H), 2.07 (s, 3 H), and 2.33 (t, $J = 8$ Hz, 2 H) ppm. The other product was identified as the *cis* isomer: n^{20}_D 1.4628; pmr (CCl₄, TMS) δ 0.87 (d, $J = 7$ Hz, 3 H), 1.0–2.0 (broad peak centered at 1.40, 12 H), and 2.33 (t, $J = 7$ Hz, 2 H) ppm. The ir spectra of

both *trans* and *cis* isomers exhibited strong bands at 2950, 2880, 1720, 1455, 1360, and 1170 cm⁻¹.

Reaction of *B*-Cyclopentyl-9-borabicyclo[3.3.1]nonane with Methyl Vinyl Ketone. *B*-Cyclopentyl-9-BBN (40 mmol) was dissolved in 40 ml of THF. To this was added 60 mmol of MVK and the reaction was followed by glpc. The reaction turned out to be quite slow. Therefore, air was introduced at the rate of 4 ml/min. After 6 hr at 25° *B*-cyclopentyl-9-BBN disappeared. Glpc examination revealed the formation of 4-cyclopentyl-2-butanone in 24% yield.

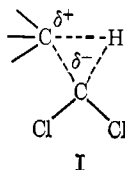
Halomethyl–Metal Compounds. LXIII. Insertion of Phenyl(bromodichloromethyl)mercury-Derived Dichlorocarbene into Benzylic Carbon–Hydrogen Bonds. Stereochemistry and Mechanism^{1,2}

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Abstract: The insertion of phenyl(bromodichloromethyl)mercury-derived dichlorocarbene into the benzylic C–H bond of (+)-2-phenylbutane occurs with predominant retention of configuration. The kinetic deuterium isotope effect for this process was determined to be 2.5. In a Hammett study, pairs of substituted cumenes, ZC₆H₄-CMe₂H (Z = *p*-CH₃, H, *p*-F, *p*-Cl, *m*-CF₃), were allowed to compete for a deficiency of PhHgCCl₂Br. These experiments demonstrated an equally good linear correlation of the log k_{rel} values with σ and σ^+ values, giving ρ values of –1.19 and –0.894, respectively. These results show that the insertion reaction in question is a concerted process in which a small partial positive charge is developed at the carbon atom into whose bond to hydrogen CCl₂ is being inserted.

In previous papers of this series we have described the insertion of dichlorocarbene derived by thermolysis of phenyl(bromodichloromethyl)mercury into C–H linkages, including those of aliphatic- and alkyl-substituted aromatic hydrocarbons,³ of aliphatic ethers,⁴ and of tetraalkyl derivatives of silicon, germanium, and tin.^{5–7} The observed relative reactivities of tertiary, secondary, and primary C–H bonds to CCl₂ insertion and the nature of the groups which activated such insertion processes (α -aryl, α -alkoxy, α -vinyl, β -trialkylmetal) led us to propose transition state I for such insertion reactions. If such a simple three-center transition state



were indeed involved, then one might expect that such

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(2) Preliminary communication: D. Seyferth and Y. M. Cheng, *J. Amer. Chem. Soc.*, **93**, 4072 (1971).

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insertion into a C–H bond involving a chiral carbon center would proceed with retention of configuration at carbon. Also, one might expect to find a linear correlation between the relative rate constants for CCl₂ insertion into XC₆H₄C–H systems and the polar substituent constants of the X substituent groups, with electron-releasing groups accelerating the insertion reaction.

In view of these expectations which were based on extensive studies of C–H insertions by CCl₂, the results of a stereochemical study by Franzen and Edens⁸ seemed rather surprising. These workers reported that insertion of CCl₂ derived from sodium trichloroacetate thermolysis into optically active 2-phenylbutane gave PhC(CH₃)(C₂H₅)CHCl₂ which was “practically inactive,” while the insertion of PhHgCCl₂-derived dichlorocarbene into this hydrocarbon gave optically inactive product. These results, however, were obtained with starting material of low optical purity, and we decided that this question of stereochemistry was of sufficient importance to warrant reinvestigation. In this paper we report the results of our further work concerning stereochemistry and mechanism of dichlorocarbene insertion into the C–H bond.

Results and Discussion

A. Stereochemistry. In view of Franzen and Edens’ report⁸ and in view of the fact that PhHgCCl₂Br reacts

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