Table II. Sensitized Ligand Isomerization in **1** and **2**[a]

Sensitizer	E_T, kcal/mol	ϕ_{isc}	Photostationary state, % trans	Quantum yields
Michler's ketone	61[b]	1.01[b]	65 ± 2.1	$\phi_{t\to c} = 0.03$ $\phi_{c\to t} = 0.04$
Zinc etioporphyrin I	41	0.9[c]	96 ± 2.9	$\phi_{t\to c} = 0.001$ $\phi_{c\to t} = 0.02$
Etioporphyrin I	40		93 ± 1.0	

[a] Butyronitrile solution, $T = 25°$. [b] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1967, p 131. [c] B. Dzhagarov, *Opt. Spektrosk.*, **28,** 66 (1970).

Photosensitization experiments with **1** and **2** as acceptors and various donors (Table II) also led to cis–trans isomerization of the 4-stilbazole as the only detectable reaction. The intense absorption of **1** and **2** at most wavelengths in the uv and visible limited the number of sensitizers that could be used without risk of singlet sensitization.[23,24] The porphyrins proved to be good sensitizers since their fluorescence was unquenched by **1** and **2** while their triplets were quenched (measured by flash spectroscopy) at rates ($k_1 = 1.8 \times 10^9$ and $k_2 = 2.4 \times 10^9$ l. mol^{-1} sec^{-1}) close to diffusion controlled. Although acceptor concentrations were high enough (1.5×10^{-3} *M*) to ensure that all sensitizer triplets were quenched for each of the sensitizers listed in Table II, quantum yields for isomerization were very low. Since triplets of **1** and **2** are not spectroscopically detectable, it is uncertain whether quenching is accompanied by efficient energy transfer.

The large variation in $D_{c/t}$ and the quantum yields with wavelengths on direct irradiation suggests that two or more isomerizable exited states are involved in the photochemistry of **1** and **2**.[25] Irradiation at 313 nm, where initial excitation is predominantly into the 4-stilbazole π–π^* transition, yields $D_{c/t} = 0.96$, a value fairly close to the value of 1.36 obtained in the direct isomerization of uncomplexed 4-stilbazole.[26] As irradiation is shifted to longer wavelengths where excitation is predominantly into the CTTL bands, $D_{c/t}$ decreases. The value $D_{c/t} = 0.004$ at 546 nm, where no direct excitation of 4-stilbazole $\pi \rightarrow \pi^*$ transitions occurs, is very close to the thermodynamic cis–trans ratio of 0.006 determined by iodine–nitrobenzene equilibration.

We suggest that isomerization initiated by irradiation of **1** and **2** at 313 nm occurs *via* the $^1\pi$–π^* state of the bound 4-stilbazole and that the isomerization initiated by longer wavelength irradiation arises from a lower energy charge-transfer state. The preferential cis → trans isomerization is reasonable for a charge-transfer state in which an electron has been transferred to an antibonding orbital of the 4-stilbazole.[27,28] It is most interesting to find so little leakage between the different excited state pathways.[29,30] This cannot be due exclusively to rapid formation of a twisted olefin state upon activation of the 4-stilbazole transitions since the quantum yields do not sum to unity. Nonradiative pathways that avoid the lower energy ^{1}CTTL* state are evidently followed. It remains to be determined whether this is a consequence of unusually short excited state lifetimes for the complex or of relatively slow rates for internal conversion between the $^1\pi$–π^* and ^{1}CTTL* states. Further studies on the reactivity of related complexes are in progress.

Acknowledgment. We thank Professor T. J. Meyer for valuable advice concerning ruthenium chemistry and the National Institutes of Health (Grant No. GM 15, 238-03,4) for support of this work.

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[23] A. B. Smith, III, and W. C. Agosta, *Chem. Commun.*, 466 (1970).

[24] E. Fischer, *J. Amer. Chem. Soc.*, **90,** 796 (1968).

[25] Since the quantum yields are relatively low, the possibility that the present results could be accounted for in terms of wavelength varying efficiency of populating one common photoreactive state cannot be excluded.

[26] Y. J. Lee, unpublished results.

[27] R. Chang and C. S. Johnson, Jr., *J. Chem. Phys.*, **46,** 2314 (1967).

[28] I. G. Lopp, R. W. Hendren, P. D. Wildes, and D. G. Whitten, *J. Amer. Chem. Soc.*, **92,** 6440 (1970).

[29] The situation regarding similar possibilities in the sensitized reaction is more complicated; discussion is deferred to the full paper.

[30] Interestingly, the present results contrast to those obtained in a study of a (*trans*-stilbenecarboxylato)cobalt(III)[4a] where extensive energy transfer was observed to dominate olefin isomerization upon irradiation of the stilbene π–π^* transitions.

[31] Alfred P. Sloan Foundation Fellow, 1970–1972.

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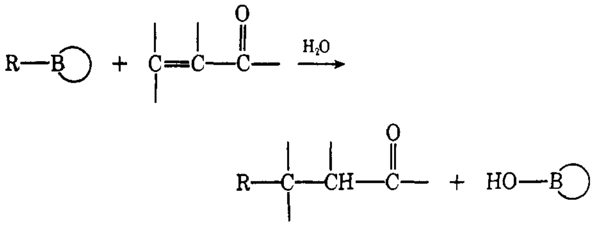
Received March 3, 1971

The Facile Reaction of *B*-Alkylboracyclanes with α,β-Unsaturated Carbonyl Derivatives. Extension of the 1,4-Addition Reaction *via* Organoboranes to Highly Branched Secondary and Tertiary Alkyl Groups

Sir:

Certain readily synthesized *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 (eq 1). This extension of the 1,4-addition reaction *via* organoboranes[1] to highly branched secondary and



$$\mathrm{R{-}B}\bigcirc + \mathrm{C{=}C{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}} \xrightarrow{\mathrm{H_2O}} \mathrm{R{-}C{-}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}} + \mathrm{HO{-}B}\bigcirc \quad (1)$$

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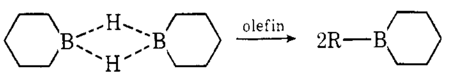
[1] (a) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Amer. Chem. Soc.*, **89,** 5708 (1967); (b) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89,** 5709 (1967); (c) H. C. Brown, G. W. Kabalka, M. W. Rathke, and M. M. Rogić, *ibid.*, **90,** 4165 (1968); (d) H. C. Brown, M. W. Rathke, G. W. Kabalka, and M. M. Rogić, *ibid.*, **90,** 4166 (1968); (e) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, E. Negishi, and S. K. Gupta, *Chem. Commun.*, 1009 (1969); (f) G. W. Kabalka, H. C. Brown, A. Suzuki, S. Honma, A. Arase, and M. Itoh, *J. Amer. Chem. Soc.*, **92,** 710 (1970); (g) H. C. Brown and G. W. Kabalka, *ibid.*, **92,** 712, 714 (1970); (h) A. Suzuki, S. Nozawa, M. Itoh, H. C. Brown, G. W. Kabalka, and G. W. Holland, *ibid.*, **92,** 3503 (1970).

tertiary alkyl groups makes this reaction broadly applicable to the formation of carbon–carbon bonds to alkyl and cycloalkyl groups of a wide range of structural types, without any known restriction.[2]

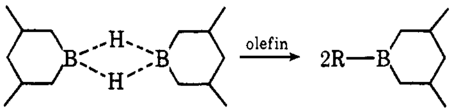
A serious limitation in applying the facile and highly general 1,4-addition reaction of organoboranes[1] has been the requirement for the fully substituted derivative, R_3B, in the reaction. It is difficult to obtain these derivatives when R is a bulky group. Thus, highly substituted olefins, such as 1-methylcyclohexene and 2,3-dimethyl-2-butene, do not undergo hydroboration to the R_3B stage.[3] All synthetic attempts to form tri-*tert*-butylborane have failed.[4]

Originally, we hoped to solve this problem by utilizing the *B*-alkyl-9-borabicyclo[3.3.1]nonanes (B-R-9-BBN). In other reactions preferential migration of the alkyl group from boron to carbon has been achieved with these derivatives.[5] However, these compounds did not solve the present problem. Evidently, in free-radical reactions, such as the 1,4 addition,[1f,g] the cyclooctyl–boron bonds possess reactivities comparable to those of the alkyl–boron bonds.[6]

We now wish to report that the above limitation can be largely overcome by using *B*-alkylborinanes,[7] *B*-alkyl-3,5-dimethylborinanes[8] (B-R-3,5-DMB-6), or *B*-alkyl-3,6-dimethylborepanes[8] (B-R-3,6-DMB-7), readily available from the hydroboration of the appropriate olefins with the corresponding hydroborating agent, bisborinane,[7] bis(3,5-dimethyl)borinane[8] (3,5-DMB-6), or bis(3,6-dimethyl)borepane[8] (3,6-DMB-7) (eq 2–4).



(2)



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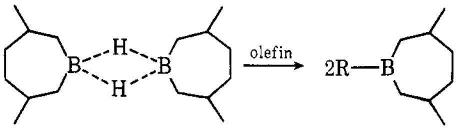
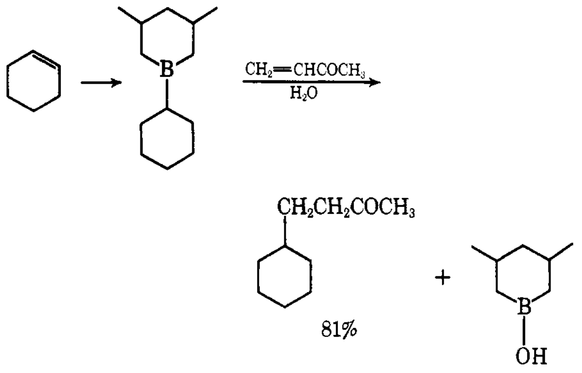


(4)

For example, the reaction of *B*-cyclohexyl-3,5-DMB-6 with methyl vinyl ketone using the standard conditions reported earlier[1a] provides the desired 4-cyclohexyl-2-butanone in 81% yield (eq 5). More important, no difficulty was encountered in applying the new procedure to the homologation of more hindered olefins, such as 1-methylcyclohexene[9] (eq 6) and 2,3-dimethyl-2-butene (eq 7).



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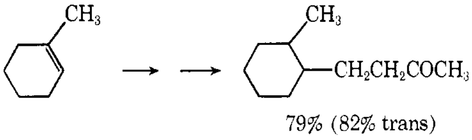
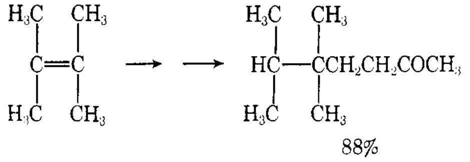


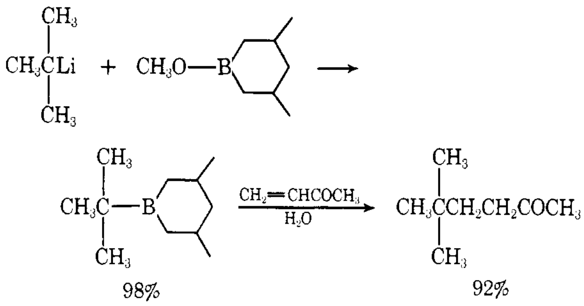
(6)



$$(CH_3)_2C{=}C(CH_3)_2 \longrightarrow \longrightarrow (CH_3)_2CH{-}C(CH_3)_2CH_2CH_2COCH_3 \quad 88\%$$

(7)

Moreover, since the reaction of the readily obtainable *B*-methoxyboracyclanes[7,8] with *tert*-alkyllithium compounds provides a convenient route to the corresponding *B*-(*tert*-alkyl)boracyclanes, as exemplified by the preparation of *B*-(*tert*-butyl)-3,5-DMB-6 in a nearly quantitative yield[10] (eq 8), it is now possible to extend the 1,4-addition reaction for the homologation of many tertiary alkyl groups not accessible *via* hydroboration.



(8)

We selected methyl vinyl ketone as a test system. However, other α,β-unsaturated carbonyl derivatives of the "inert" type,[1g] such as 3-pentenone and 2-cyclohexenone, proved to be equally applicable.

The experimental results are summarized in Table I.

Although use of *B*-alkylborinanes gives satisfactory results, as shown in Table I, the preparation of bisborinane, the hydroborating agent for the synthesis of *B*-alkylborinanes, requires an isomerization of the organoborane intermediate at an elevated temperature (170°).[7] Therefore, the more readily accessible *B*-alkyl-3,5-DMB-6 and *B*-alkyl-3,6-DMB-7[8] appear preferable.

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(2) In contrast to the organoborane route, the related 1,4 addition *via* copper-catalyzed Grignard reagents or organocopper derivatives does not appear to have been applied successfully to any aldehydes or to ketones not containing a substituent in the β position; G. H. Posner, *Org. React.*, in press.

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

(4) G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *J. Amer. Chem. Soc.*, **79**, 5190 (1957).

(5) (a) H. C. Brown, E. F. Knights, and R. A. Coleman, *ibid.*, **91**, 2144 (1969); (b) H. C. Brown and R. A. Coleman, *ibid.*, **91**, 4606 (1969); (c) H. C. Brown and M. M. Rogić, *ibid.*, **91**, 2146, 4304 (1969); (d) H. C. Brown, M. M. Rogić, H. Nambu, and M. W. Rathke, *ibid.*, **91**, 2147 (1969); (e) H. C. Brown, H. Nambu, and M. M. Rogić, *ibid.*, **91**, 6852, 6854, 6855 (1969).

(6) For example, the reaction of *B*-cyclopentyl-9-borabicyclo[3.3.1]-nonane with methyl vinyl ketone provided only a 24% yield of 4-cyclopentyl-2-butanone, although all of the starting borane disappeared.

(7) H. C. Brown and E. Negishi, *J. Organometal. Chem.*, **26**, C67 (1971).

(8) H. C. Brown and E. Negishi, *ibid.*, **28**, C1 (1971).

(9) 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^{20}D (trans) 1.4568 and n^{20}D (cis) 1.4628).

(10) The procedure is based on the work in progress with G. W. Kramer on the preparation of *B*-alkyl-9-BBN.

Table I. The Reaction of the *B*-Alkylboracyclanes with α,β-Unsaturated Carbonyl Derivatives

Alkyl group of *B*-alkyl-boracyclane	α,β-Unsaturated carbonyl derivative[a]	Product[b]	Yield,[c] % 3,5-DMB-6[d]	 3,6-DMB-7[e]	 Borinane[f]
sec-Butyl	MVK	5-Methyl-2-heptanone	83 (75)[g]	80	74 (67)[6]
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		
trans-2-Methyl-cyclohexyl	MVK	4-(2′-Methylcyclo-hexyl)-2-butanone[h]	79 (73)[g]		
exo-Norbornyl	MVK	4-Norbornyl-2-butanone[i]	81	61	65
tert-Butyl	MVK	5,5-Dimethyl-2-hexanone	90 (76)[g]		
tert-Butyl	CH	3-(*tert*-Butyl)-cyclohexanone	73		
2,3-Dimethyl-2-butyl	MVK	5,5,6-Trimethyl-2-heptanone	88 (81)[g]	51	75 (71)[g]
n-Hexyl	MVK	2-Decanone[j]	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-DMB-6. [e] Using *B*-alkyl-4,6-DMB-7. [f] Using *B*-alkylborinane. [g] Numbers in parentheses are isolated yields. [h] See ref 9. [i] A single compound by glpc. Presumably the exo isomer. [j] Contaminated with 3% of an isomeric product.

The yield of a desired product is usually higher when the corresponding *B*-alkyl-3,5-DMB-6 is employed (Table I). However, this advantage may be somewhat offset, at present, by the higher cost of the starting diene, 2,4-dimethyl-1,4-pentadiene. In any event, 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. Although the latter advantage of the present procedure does not extend to primary alkyl groups, this procedure does have the advantage of yielding purer products, with only small amounts of the minor isomer. For example, in the case of 1-hexene, the isomeric purity of the product is much higher (97%) than the earlier figure of 85% realized in the reaction of trialkylboranes from 1-butene and 1-octene with methyl vinyl ketone.[1a]

Isolation of the desired products offered no difficulty. Simple distillation of the reaction mixture was usually sufficient. In cases in which the *B*-hydroxyboracyclanes interfered with the distillation, this difficulty could be avoided by oxidation of the product with 30% hydrogen peroxide and 3 *N* sodium hydroxide prior to distillation.

The following procedure for the preparation of 5,5,6-trimethyl-2-heptanone from 2,3-dimethyl-2-butene is representative. *B*-Thexyl-3,5-DMB-6 was prepared as reported previously[8] by the addition of 3.36 g (40 mmol) of 2,3-dimethyl-2-butene to 25 ml (25 mmol) of a 1 *M* solution of bis(3,5-dimethyl)borinane in THF. After destroying the residual hydride with 1.8 ml (100 mmol) of water, 4.2 g (60 mmol) of methyl vinyl ketone and 2.26 g (10 mmol) of *n*-hexadecane (internal standard) were added and the reaction mixture was stirred overnight at 25°. Glpc examination of the reaction mixture 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-DMB-6. 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); $n^{20}\text{D}$ 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.

In view of the fact that an increasing number of reactions of organoboranes involve free-radical mechanisms, it seems likely that application of the presently described *B*-alkylboracyclanes in such reactions, in place of simple trialkylboranes, will provide improvements similar to the present results.[11]

(11) H. C. Brown and M. M. Midland, *J. Amer. Chem. Soc.*, **93**, 3291 (1971).

(12) Postdoctoral Research Associate on Grant No. DA 31-124 ARO(D) 453, supported by the U. S. Army Research Office (Durham).

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Received February 20, 1971

A New Photoproduct of Cytosine. Structure and Mechanism Studies[1,2]

Sir:

We have characterized derivatives of a homoadduct of cytosine isolated from the irradiation (254 nm) of

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(1) This publication is identified as NYO-2798-61; the detailed article will appear elsewhere: D. F. Rhoades, and S. Y. Wang, *Biochemistry*, in press.

(2) This investigation was supported in part by Contract No. AT-(30-1)-2798 of the U. S. Atomic Energy Commission, and by a Public Health Service Research Career Development Award (K3-GM-4134) from NIGMS.