(3) C. M. Deber, V. Madison, and E. R. Blout, *Acc. Chem. Res.*, **9**, 106 (1976).
(4) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).
(5) For general reviews see (a) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972); (b) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974); (c) D. J. Cram and J. M. Cram, *Science*, **183**, 803 (1974); (d) G. W. Gokel and H. D. Durst, *Synthesis*, 168 (1976).
(6) Burdick and Jackson Labs, Muskegon, Mich.
(7) R. G. Ghirardelli, *J. Am. Chem. Soc.*, **95**, 4987 (1973).
(8) P. R. Mallinson and M. R. Truter, *J. Chem. Soc., Perkin Trans. 1*, 1818 (1972).
(9) J. J. Dechter and J. I. Zink, *J. Am. Chem. Soc.*, **98**, 845 (1976).

Mark P. Mack, Richard R. Hendrixson
Richard A. Palmer,* Robert G. Ghirardelli*
Paul M. Gross Chemical Laboratory, Duke University
Durham, North Carolina 27706

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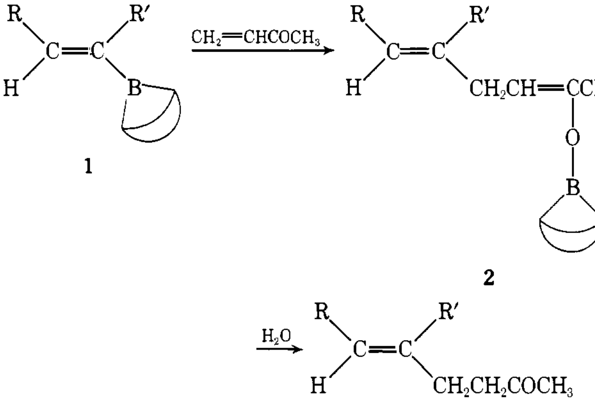
Conjugate Addition of *B*-Alkenyl-9-borabicyclo[3.3.1]nonanes to Methyl Vinyl Ketone. A Convenient Synthesis of γ,δ-Unsaturated Ketones

Sir:

B-Alkenyl-9-borabicyclo[3.3.1]nonanes (*B*-alkenyl-9-BBN) (**1**), readily prepared by the hydroboration of acetylenes with 9-BBN,[1] undergo a smooth 1,4-addition to methyl vinyl ketone (MVK) and related ketones in refluxing tetrahydrofuran. Hydrolysis of the initially formed enol borinate intermediate (**2**) provides the corresponding 4-alkenyl-2-butanones (**3**) (eq 1).



1

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(1)

3

An important application for organocopper derivatives is their conjugate addition to α,β-enones.[2] Regretfully, easily polymerizable α,β-enones, such as methyl vinyl ketone, are not readily accommodated in this reaction.[3,4] However, the free radical addition of organoboranes to α,β-enones readily accommodates methyl vinyl ketone and related derivatives.[5]

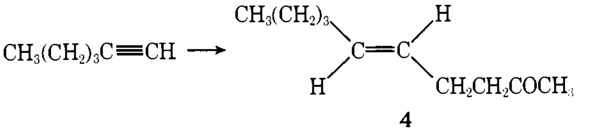
It would be highly desirable to extend such conjugate additions to the introduction of the vinyl group. Unfortunately, we have been unsuccessful in extending such conjugate additions to derivatives containing such groups. For example, our efforts to induce a free radical addition of *trans*-1-hexenyldiphenylborane to methyl vinyl ketone have failed.

Hooz and Layton were successful in achieving a conjugate addition with diisobutyl-*trans*-1-hexenylalane to α,β-enones.[4] However, even here they achieved their best yield, 67%, with stabilized substituted α,β-enones, such as benzalacetone. The optimum yield with methyl vinyl ketone was only 30%. They noted that the reaction proceeds satisfactorily only with cisoid enones (i.e., those ketones capable of adopting a cisoid conformation); transoid enones, such as 2-cyclohexenone, gave only complex mixtures not containing the desired product.

In the course of our efforts to achieve a free radical addition of vinylborane derivatives, we observed a new thermal reaction, one which led to the same product. It appears to be related to the reaction developed by Hooz and Layton in giving the same stereochemistry and in accommodating only cisoid enones. However, it gave greatly improved yields with methyl vinyl ketone. Since this particular derivative had proven to be a major stumbling block for previous workers, we decided to explore the range of applicability of various vinyl derivatives utilizing this labile reagent.

The conjugate addition reaction of alkenylboranes appears to be one of wide generality (Table I). A variety of structural modifications on the vinylic unit can be accommodated, including the presence of a heteroatom (eq 2-8).

We utilized *B*-1-hexenyl-9-BBN in a brief exploration of the applicability of this reaction to other α,β-enones (**11–14**). The cisoid ketones, **11** and **12**, reacted satisfactorily to give the



(2)

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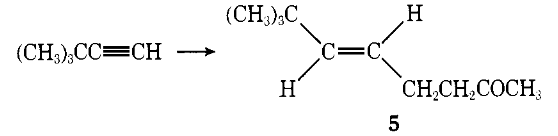

(3)

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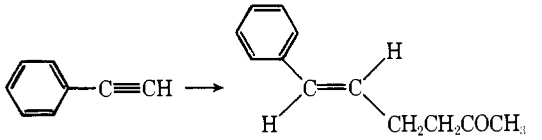

(4)

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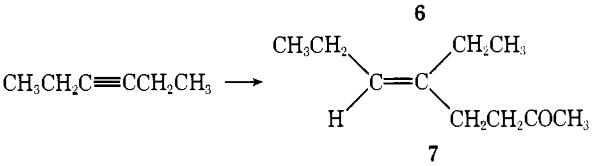

(5)

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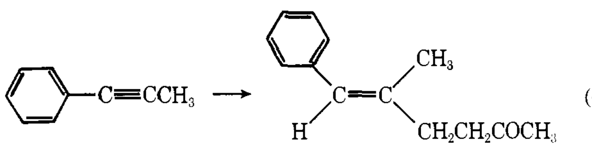
Table I. Conversion of Alkynes into 4-Alkenyl-2-butanones by the Reaction of the Corresponding *B*-Alkenyl-9-BBN Derivatives with Methyl Vinyl Ketone

Alkyne	Product[a]	Yield,[b] %	n^{20}D	Semicarbazone, mp (°C)
1-Hexyne[d]	*trans*-5-Decen-2-one (**4**)	87	1.4540	74.5-75.5
3,3-Dimethyl-1-butyne[e]	7,7-Dimethyl-*trans*-5-octen-2-one (**5**)	(85)[c]	1.4355	132.5-133.5
Phenylethyne[f]	*trans*-6-Phenyl-5-hexen-2-one (**6**)	93	1.5451	127-128
3-Hexyne[e]	5-Ethyl-*trans*-5-octen-2-one (**7**)	35	1.4460	129-130
1-Phenyl-1-propyne[f]	5-Methyl-*trans*-6-phenyl-5-hexen-2-one (**8**)	62	1.5400	144-145
5,5-Dimethyl-2-pentyne[e]	5,7,7-Trimethyl-*trans*-5-octen-2-one (**9**)	69	1.4456	133-134
5-Chloro-1-pentyne[g]	9-Chloro-*trans*-5-nonen-2-one (**10**)	66	1.4695	

[a] Satisfactory IR, ^{1}H NMR, and high resolution mass spectral data were obtained for all new compounds. [b] Yield by GLC analysis based on 9-BBN. [c] Isolated yield. [d] Distilled *B*-1-hexenyl-9-BBN was used. [e] A 10% excess of the alkyne was used. [f] A 50% excess of alkyne was used. [g] A 100% excess of alkyne was used. With straight-chain terminal alkynes, the excess is required to minimize double hydroboration.



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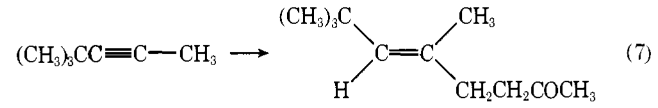
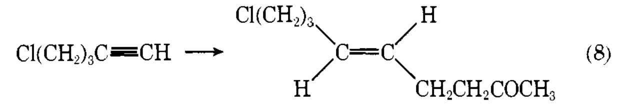
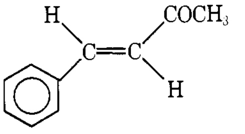


9 (7)

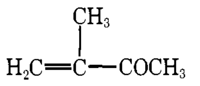


10 (8)

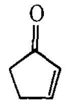
desired products in the indicated yields; the transoid ketones, **13** and **14**, gave complex mixtures in which we failed to find the desired products.



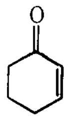
11, 90%



12, 50%

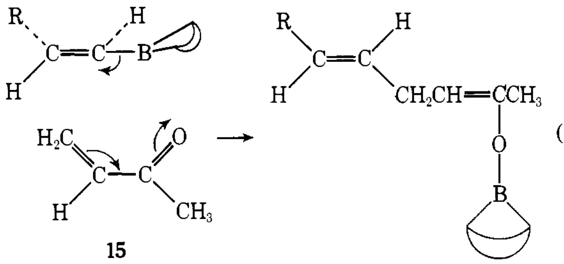


13, 0%



14, 0%

These results are consistent with a process (eq 11) which proceeds via a cyclic species (**15**), transferring the vinyl group from boron to carbon with retention of its stereochemistry, giving the intermediate **16**, which is hydrolyzed to the desired product (eq 1).



(11)

15

16

The reaction evidently involves a regio- and stereospecific replacement of boron by carbon. Thus, the hydroboration of a terminal acetylene provides the pure trans alkenyl derivative.[7] In each case only a single product was indicated by the NMR and GC examination. All of the product obtained from the reaction of *trans*-1-alkenyl-9-BBN derivatives with methyl vinyl ketone exhibited a strong band at ~970 cm^{-1} in their infrared spectra, indicating a trans disubstituted olefinic linkage.[8] We undertook to confirm the conclusion that these reactions proceed with retention by reducing[9] **4** to 5-decene. In synthetic mixtures, we could detect 1% *cis*-5-decene in 99% trans. However, in the product from **4** there was no measurable trans detected.

The following procedure for the preparation of 7,7-dimethyl-*trans*-5-octen-2-one is representative. To an oven-dried nitrogen-flushed 500-ml flask equipped with a reflux condenser and magnetic stirring bar was added 208 ml of 0.48 M 9-BBN[10] (100 mmol) in THF. The solution was cooled in an ice-water bath, and 9.1 g (110 mmol) of 3,3-dimethyl-1-butyne was added over 5 min. The mixture was then stirred overnight at room temperature to ensure complete hydroboration. Methyl vinyl ketone (7.7 g, 110 mmol) was added, and the solution was heated under reflux for 16 h.[11] After cooling to room temperature, the residual organoborane was oxidized by adding 3 N sodium hydroxide (40 ml), followed by the slow addition of 40 ml of 30% hydrogen peroxide (*Caution:* exothermic). The reaction mixture was maintained at 50 °C for 1 h to ensure complete oxidation. The aqueous layer was saturated with anhydrous potassium carbonate, separated, and extracted with hexane. After drying over anhydrous magnesium sulfate, the combined organic layer was distilled to provide 13.1 g (85%) of 7,7-dimethyl-*trans*-5-octen-2-one: bp 80-82 °C (12 mm); $n^{20}{}_{\mathrm{D}}$ 1.4355; semicarbazone mp 132.5-133.5 °C; IR (neat) 1720, 975 cm^{-1}; ^{1}H NMR (CCl$_4$, Me$_4$Si) δ 0.95 (s, 9 H), 2.05 (s, 3 H), 2.2-2.4 (m, 4 H), 5.4 (m, 2 H).

It is evident that this procedure makes it practical to achieve the conjugate addition of vinyl groups stereospecifically to methyl vinyl ketone and related derivatives. Perhaps even more important is the evident opening up of a new reaction path for the utilization of organoborane derivatives with their unique and valuable characteristics[7] for synthetic applications.

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References and Notes

(1) H. C. Brown, E. F. Knights, and C. G. Scouten, *J. Am. Chem. Soc.*, **96**, 7765 (1974); C. G. Scouten, Ph.D. Thesis, Purdue University, West Lafayette, Ind., 1974.
(2) G. H. Posner, *Org. React.*, **19**, 1 (1972).
(3) S. Danishevsky and B. H. Migdalof, *Chem. Commun.*, 1107 (1969).
(4) J. Hooz and R. B. Layton, *Can. J. Chem.*, **51**, 2098 (1973). For conjugate additions involving a vinylcopper complex, see J. Hooz and R. B. Layton, *Can. J. Chem.*, **48**, 1626 (1970).
(5) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 5708 (1967); H. C. Brown and G. W. Kabalka, *ibid.*, **92**, 712, 714 (1970).
(6) Unpublished research of Peyton Jacob III.
(7) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972; H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley, New York, N.Y., 1975.
(8) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds", Wiley, New York, N.Y., 1967, p 108.
(9) R. O. Hutchins, B. E. Maryanoff, and C. A. Milewski, *J. Am. Chem. Soc.*, **93**, 1793 (1971).
(10) Solid 9-BBN and solutions of 9-BBN in THF are available from the Aldrich Chemical Co., Milwaukee, Wis.
(11) In most cases, the maximum yield was reached after 3-4 h, but it was often convenient to allow the reaction mixture to reflux overnight.
(12) For example, the addition of small amounts of oxygen, which catalyzes the conjugate addition of trialkylboranes to α,β-unsaturated ketones,[5] did not induce a reaction between *trans*-1-hexenyldiphenylborane and methyl vinyl ketone. Similarly, catalytic quantities of oxygen did not result in any observable change in the rate of reaction of *B-trans*-1-hexenyl-9-BBN with methyl vinyl ketone. Nor did the presence of small amounts of iodine, a known inhibitor for free radical reactions of organoboranes,[13] have any effect.
(13) M. M. Midland and H. C. Brown, *J. Am. Chem. Soc.*, **93**, 1506 (1971).
(14) Graduate research assistant on grants provided by the National Science Foundation (GP-27742X) and by G. D. Searle and Company, Chicago, Ill.

Peyton Jacob, III,[14] Herbert C. Brown*
Richard B. Wetherill Laboratory, Purdue University
West Lafayette, Indiana 47907

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Hydride Transfer Reactions. Oxidation of *N*-Methylacridan by 1,4-Benzoquinone and Related π Acceptors

Sir:

Oxidations of dihydropyridines and related compounds by hydride acceptors are of interest as models for biological oxidation-reduction reactions involving the pyridine nucleotide coenzymes,[1] and as reactions of π donors with π acceptors.[2]