Table II. Synthesis of Conjugated Enynes via Terminal Alkenylcopper Coupling to 1-Bromo-1-hexyne

alkenylborane	product[a]	GC yield,[b] %
B-[(1E)-1-hexen-1-yl]-9-BBN	(5E)-5-dodecen-7-yne	93
B-[(1E)-3,3-dimethyl-1-buten-1-yl]-9-BBN	(3E)-2,2-dimethyl-3-decen-5-yne	90 (81)
B-[(1E)-1-(5-chloropenten)-1-yl]-9-BBN	(4E)-1-chloro-4-undecen-6-yne	98 (75)

[a] Satisfactory ^{1}H NMR, ^{13}C NMR, IR, and exact mass spectral analyses were obtained for all products. [b] Isolated yields in parentheses refer to analytically pure material.

°C. The reaction was quenched by the addition of 5 mL of 1 N HCl. The organic phase was then transferred via a double-ended needle to a separate flask and the remaining aqueous phase was washed with three 5-mL portions of Et_2O. The volatiles were removed in vacuo (60 mmHg) from the combined organic extracts and 25 mL of pentane was added. This was followed by the addition of 1 mL of ethanolamine, which precipitated the borane byproduct formed in the reaction. The resulting slurry was centrifuged, and an aliquot was taken from the supernatant and analyzed by GC. There was present 90% (3E)-2,2-dimethyl-3-decen-5-yne, >97% pure. The product was isolated in the following manner. After the supernatant was removed from the solid, the solution was washed with water and then dried over $MgSO_4$. The pentane was removed in vacuo and the product was distilled [bp 62–64 °C (1.7 mmHg)] to provide 1.30 g (81%) of a clear, colorless liquid, which was analytically pure by GC analysis: n^{20}_D 1.4666; ^{1}H NMR ($CDCl_3$) δ 6.09 (d, J = 16 Hz, 1 H), 5.35 (dt, J = 16, J = 2 Hz, 1 H), 2.4–2.0 (m, 2 H), 1.8–1.2 (m, 4 H), 1.01 (s, 9 H), 1.0–0.7 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 153.06, 105.90, 88.76, 79.48, 33.72, 31.25, 29.25, 22.12, 19.19, 13.63; IR (neat) 2230, 1785, 1465, 1365, 1270, 1200, 1165, 965 cm^{-1}; exact mass spectral analysis calculated for $C_{12}H_{20}$ 164.156, found 164.156.

Thus, alkenylcopper intermediates generated from B-alkenyl-9-BBN readily undergo cross-coupling with 1-halo-1-alkynes in a highly stereospecific manner. A convenient workup procedure allows the isolation of crude products, >95% pure, in nearly quantitative yields. Analytically pure products are obtained upon simple distillation. The stereochemistry of the conjugated enyne is predefined by the stereochemistry of the starting alkenylborane. The mildness of the method promises to permit the use of a variety of sensitive functional groups. At the present time, we are exploring the extension of this reaction to other, perhaps more versatile, alkenyldialkylboranes and the use of the reaction in the synthesis of various insect pheromones.

Acknowledgment. We are grateful to Albany International Chemicals Division for their financial support of this work.

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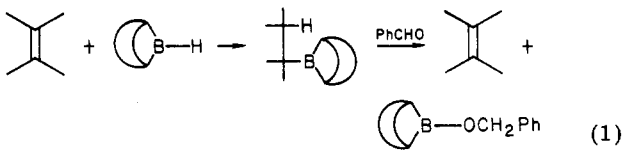
Received August 12, 1980

Synthesis of Methylenecycloalkanes from Cycloalkenes via Borane Chemistry

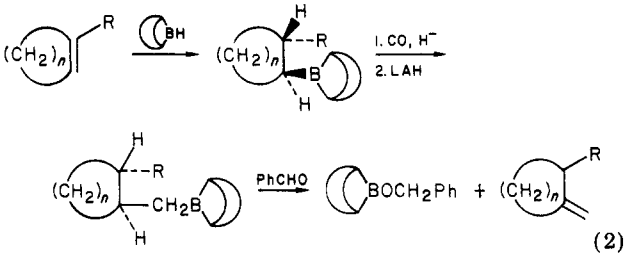
Summary: B-(Cycloalkylmethyl)-9-BBN derivatives, now readily available through the homologation reaction,[1] are convenient substrates for the synthesis of exocyclic methylene compounds. The method appears to be general. Moreover, since the synthesis proceeds from the cycloalkene, it provides a valuable alternative to the customary methylenation of carbonyl compounds by the Wittig and related procedures. The method also provides a clean synthesis of deuterium-labeled compounds without positional scrambling or loss of label.

Sir: The scope and utility of the phosphorane route to exocyclic olefins is well documented.[2] The method does have limitations, however, and several workers have proposed alternatives to overcome problems, such as steric hindrance, enolization, and epimerization.[3]

Midland and co-workers have recently shown[4] that B-alkyl-9-BBN derivatives undergo a facile reaction with aldehydes to generate olefins (eq 1). This reaction, coupled with our recently developed synthesis of B-(cycloalkylmethyl)-9-BBN derivatives[1] via carbonylation–reduction, provides an alternative method for methylenecycloalkane synthesis (eq 2).



(1)

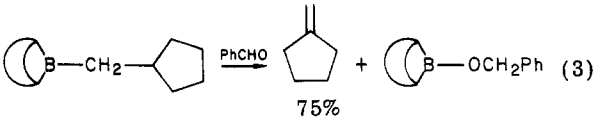


(2)

R = H, alkyl

The method is limited to those substrates which hydroborate regioselectively (or which are symmetrical), but the high stereospecificity of the reaction of 9-BBN with olefins should provide compounds unavailable by other methods.

Thus, B-(cyclopentylmethyl)-9-BBN reacts with benzaldehyde in refluxing THF with a half-life of less than 10 min to give a 75% yield of methylenecyclopentane (eq 3).



(3)

75%

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(2) Maercker, A. *Org. React.* **1965**, *14*, 270. Johnson, A. W. "Ylid Chemistry"; Academic Press: New York, 1966.
(3) (a) Brady, W. T.; Patel, A. D. *Synthesis* **1972**, 565. (b) Coates, R. M.; Sowerby, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 4758. (c) Johnson, C. R.; Shanklin, J. R.; Kirchhoff, R. A. *Ibid.* **1973**, *95*, 6462. (d) Hata, Y.; Wanatabe, M. *Ibid.* **1973**, *95*, 8450. (e) Hasselmann, D. *Chem. Ber.* **1974**, *107*, 3486. (f) Meyers, A. I.; Ford, M. E. *Tetrahedron Lett.* **1975**, 2861. (g) Watanabe, Y.; Shiono, M.; Mukaiyama, T. *Chem. Lett.* **1975**, 871. (h) Oshima, K.; Takai, K.; Hotta, Y.; Nozaki, H. *Tetrahedron Lett.* **1978**, 2417.
(4) Midland, M. M.; Tramontano, A.; Zderic, S. A. *J. Organomet. Chem.* **1978**, *156*, 203.

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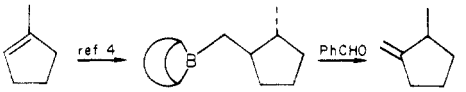
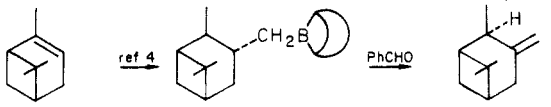
The reaction is aided[4] by the rate acceleration of the tertiary β-hydrogen common to these substrates. In addition, we have noted a moderate increase in rate when the reaction is performed under neat conditions. The absence of solvent greatly assists the isolation of the products, particularly important for the more volatile cases.

Thus, treatment of crude [*trans*-(2-methylcyclopentyl)methyl]-9-BBN with 1 equiv of benzaldehyde, followed by bulb-to-bulb distillation in vacuo, provides 2-methylmethylenecyclopentane in an overall yield of 65% (eq 4).



65% (4)

The clean stereospecificity of the process is demonstrated by the following example (eq 5). The isomeric

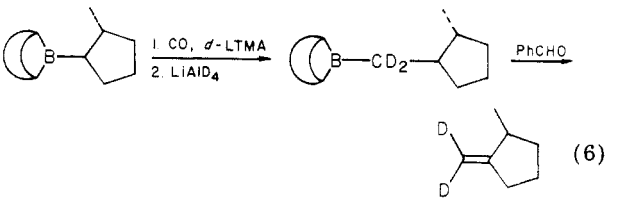


$[\alpha]^{21}_D$ −48.8 $[\alpha]^{23}_D$ +20.4 ($CDCl_3$) (5)

purity was 100% within the limits of detection by ^{13}C NMR.[5] Methylenation of isopinocamphone, on the other hand, would undoubtedly result in serious epimerization (under basic conditions) or rearrangement (under acidic conditions).

The method also appears to be well suited to the preparation of deuterium-labeled compounds, using the relatively inexpensive lithium aluminum deuteride as the sole source of deuterium. Although methods do exist for the synthesis of methylene-d_2-cycloalkanes,[2b,2e,6] these are all low yield and/or cumbersome. The Wittig method itself leads to loss of label and scrambling.[3b,6a,c]

Our method provides a good yield of isotopically pure product. Thus, when *B*-(2-methylcyclopentyl)-9-BBN is carbonylated [$Li(MeO)_3AlD$], reduced ($LiAlD_4$), and reacted with benzaldehyde, a 52% isolated yield of 2-methylmethylene-d_2-cyclopentane is obtained (eq 6).



(6)

Registry No. *B*-(Cyclopentylmethyl)-9-BBN, 74763-89-6; methylenecyclopentane, 1528-30-9; [*trans*-2-(methylcyclopentyl)methyl]-9-BBN, 74763-94-3; 2-methylmethylenecyclopentane, 41158-41-2; (−)-2-pinene, 7785-26-4; (+)-3-methylenepinane, 76094-32-1; 2-methylmethylene-d_2-cyclopentane, 76036-48-1.

(5) **3**: NMR ($CDCl_3$, Me_4Si) 149.9, 110.2, 46.9, 42.0, 40.3, 39.4, 36.2, 34.0, 27.8, 22.1, 21.2.

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(7) Postdoctoral research assistant on Grant CHE 76-20846 provided by the National Science Foundation.

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Received August 12, 1980