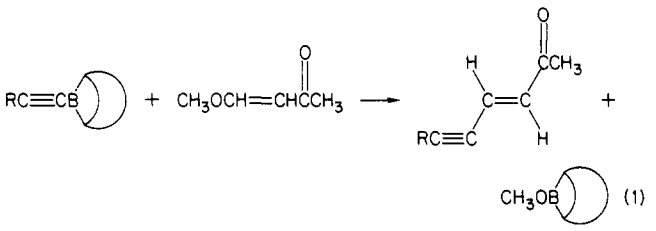
## Conjugate Addition-Elimination in the Reaction of *B*-1-Alkenyl-9-borabicyclo[3.3.1]nonanes with 4-Methoxy-3-buten-2-one. A Convenient New Route to Conjugated Dienones

*Summary:* *B*-1-Alkenyl-9-borabicyclo[3.3.1]nonanes (*B*-1-alkenyl-9-BBN), easily and quantitatively prepared by the reaction of 9-BBN with various alkynes, undergo a facile reaction with the commercially available 4-methoxy-3-buten-2-one in diethyl ether at room temperature to provide conjugated dienones in essentially quantitative yields.

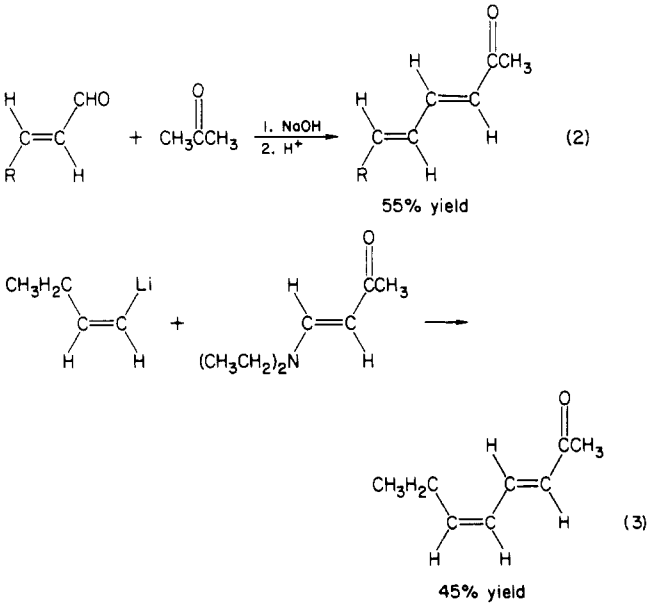
*Sir:* Recently we described the conjugate addition–elimination reaction of *B*-1-alkynyl-9-BBN (*B*-1-alkynyl-9-borabicyclo[3.3.1]nonanes) to 4-methoxy-3-buten-2-one and related derivatives to provide excellent yields of the corresponding conjugated enynones (eq 1).[1] We have



(1)

noted a great similarity between the reactivity of alkenyldialkylboranes and their alkynyldialkylborane counterparts. This reactivity is often in marked contrast to that of saturated trialkylboranes. Consequently, we undertook to determine whether the alkenyl-9-BBN compounds would undergo a conjugate addition–elimination reaction to produce conjugated dienones.

Conjugated dienones are found in nature[2] and are generally synthesized in one of two ways. The first involves the condensation of a conjugated aldehyde with acetone, followed by elimination of the resulting alcohol[3] (eq 2). The second method is by the Benary reaction[4] (eq 3).



(2)

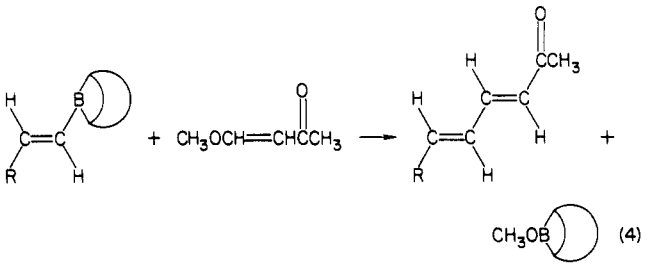
55% yield

(3)

45% yield

Although both methods are apparently highly stereospecific and can be carried out with relative ease, a significant improvement in the modest yields is clearly a desirable objective.

Therefore, we sought to develop the conjugate addition–elimination reaction of alkenyldialkylboranes to provide an alternative synthesis of these highly functionalized dienones (eq 4), hopefully in markedly improved yields.



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Indeed, we found that the reaction proceeds with relative ease for a variety of *B*-1-alkenyl-9-BBN compounds to provide the corresponding conjugated *trans,trans*-dienones in quantitative yields (Table I).

**Table I. Preparation of Conjugated *trans,trans*-Dienones[a]**

| alkenylborane | product | GC yield,[b] % |
|---|---|---|
| *B-trans*-1-nonen-1-yl-9-BBN | *trans,trans*-3,5-tridecadien-2-one | 100 (95) |
| *B-trans*-1-octen-1-yl-9-BBN | *trans,trans*-3,5-dodecadien-2-one | 98 |
| *B-trans*-3,3-dimethyl-1-buten-1-yl-9-BBN | *trans,trans*-7,7-dimethyl-3,5-octadien-2-one | 99 |
| *B-trans*-1-(5-chloropenten)-1-yl-9-BBN | *trans,trans*-9-chloro-3,5-nonadien-2-one | 100 |

[a] All reactions were run in diethyl ether for 24 h at 25 °C and hydrolyzed with ethanolamine. A 20% excess of 4-methoxy-3-buten-2-one was utilized in all cases. [b] Isolated yield in parentheses, >95% pure. Satisfactory IR, $^1$H NMR, and exact mass spectral analyses were obtained.

The reactions can be carried out by utilizing distilled *B*-1-alkenyl-9-BBN, or by preparing and utilizing the borane prepared in situ (using 1 equiv of 9-BBN and 2.25 equiv of 1-alkyne).[5] In both cases the yields of conjugated dienone is quantitative.

The reactions are complete after 24 h at room temperature in diethyl ether. As in the case of the *B*-1-alkynyl-9-BBN compounds,[1] the reaction can be monitored by $^{11}$B NMR. Thus the appearance of *B*-methoxy-9-BBN and concurrent disappearance of *B*-1-alkenyl-9-BBN is strong evidence that the reaction proceeds by a conjugate addition–elimination mechanism through a six-membered transition state.

The *B*-methoxy-9-BBN byproduct was readily removed from the desired product by precipitation of its ethanolamine adduct.[6] This provided essentially pure (≥95%) material without the need for further purification of the crude material.

The method is highly stereoselective, providing *trans,trans*-dienones to the exclusion of other isomers within the limits of detection of 360-MHz $^1$H NMR.[4]

The following procedure for the preparation of *trans,trans*-3,5-tridecadien-2-one is representative. A dry, nitrogen-flushed, 25-mL centrifuge tube equipped with a Teflon-coated magnetic stirring bar and capped with a rubber septum was charged with 2.46 g (10 mmol) of *B-trans*-1-nonen-1-yl-9-BBN, 0.34 g (3 mmol) of *n*-octane as

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(2) Renold, W.; Näf-Müller, R.; Keller, U.; Willhalm, B.; Ohloff, G. *Helv. Chim. Acta* **1974**, *57*, 1301.
(3) (a) Surber, W.; Thens, V.; Colombi, L.; Schinz, H. *Helv. Chim Acta* **1956**, *39*, 1299. (b) Grünanger, P.; Grieco, P. *Gazz. Chim. Ital.* **1958**, *88*, 296.
(4) Näf, F.; Decorzant, R. *Helv. Chim. Acta* **1974**, *57*, 1309.
(5) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96.
(6) Kramer, G. W.; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 2292.

0022-3263/84/1949-5024$01.50/0 

internal standard, and 7.6 mL of anhydrous diethyl ether. To the resulting solution was added 1.2 g (12 mmol) of 4-methoxy-3-buten-2-one.[7] The reaction mixture was stirred for 24 h at 25 °C and then quenched with 0.61 g (10 mmol) of ethanolamine. A precipitate of 9-BBN–ethanolamine adduct was formed almost immediately. After the resulting slurry was stirred for 1 h, the reaction mixture was centrifuged. Analysis of the supernatant by GC revealed that *trans,trans*-3,5-tridecadien-2-one was formed in 100% yield.[8] The supernatant was decanted from the solid and the volatiles were removed in vacuo. There remained 1.85 g (95%) of *trans,trans*-tridecadien-2-one, >95% pure by GC.[8] An analytically pure sample was obtained by preparatory GC:[8] IR (neat) 1685, 1667, 1630, 1592, 1250, 995 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, $Me_4Si$) $\delta$ 0.6–1.0 (t, 3 H), 1.0–2.0 (m, 10 H), 1.9–2.4 (m, 2 H), 2.23 (s, 3 H), 5.9–6.3 (m, 3 H), 6.9–7.3 (m, 1 H); $^{13}C$ NMR ($CDCl_3$, $Me_4Si$) $\delta$ 198.34, 145.57, 143.85, 129.01, 128.89, 33.20, 32.28, 31.89, 29.22, 28.86, 27.12, 22.70, 14.08; exact mass calcd for $C_{13}H_{22}O$ 194.167, found 194.167.

An exploratory experiment under the same conditions attempting to utilize the organoborane from 3-hexyne and 9-BBN failed to yield the desired product. We did not attempt to force the reaction by utilizing more drastic conditions.

**Acknowledgment.** We thank ChemSampCo, Inc., and the National Institutes of Health (Grant GM-10937) for their generous financial support of this work.

(7) The reagent is available from Aldrich Chemical Co., distilled prior to use, bp 70 °C (15 mmHg).

(8) GC analyses were carried out with a Hewlett-Packard 5750 chromatograph using a 6 ft × 0.25 in. column packed with 10% SE-30 on Chromosorb W. For preparative GC, a 6 ft × 0.5 in. column packed with 10% SE-30 on Chromosorb W was used.

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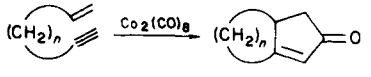
## Synthesis of the Angularly Fused Triquinane Skeleton via Intramolecular Organometallic Cyclization

*Summary:* Preparation and cyclization of 5-pentynyl-1-cyclopentene to tricyclo[6.3.0.$0^{4,8}$]undec-1-en-3-one with $Co_2(CO)_8$ followed by conversion to a bisnorisocomene are described. Isocomene itself is not accessible in reasonable yield by this route, however.

*Sir:* In 1981 we reported[1] the first intramolecular examples (eq 1) of the $Co_2(CO)_8$-promoted cyclopentenone preparation discovered a decade ago by Pauson and Khand.[2]



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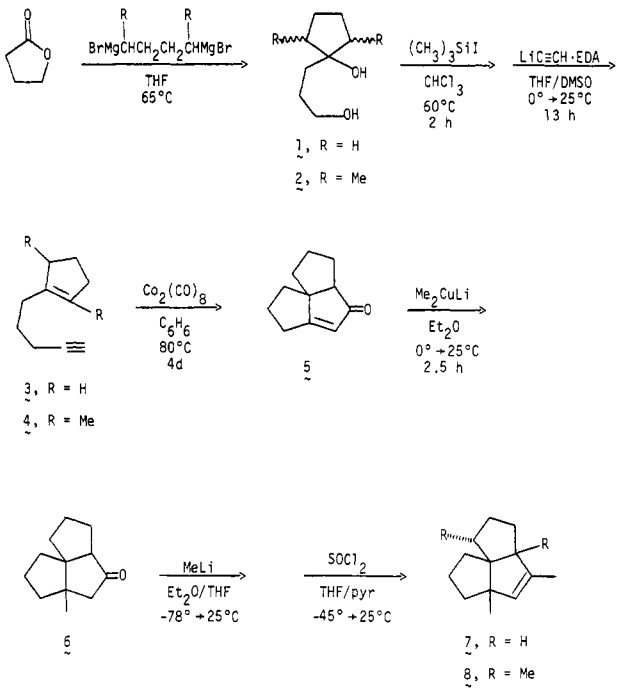
Very recently Magnus and co-workers have described the elaboration of this methodology to the total synthesis of coriolin, a linearly fused triquinane.[3] We report herein the first attempts to extend this process to the *angularly* fused triquinane system, using synthetic schemes *which completely avoid the use of carbocyclic starting materials.* Scheme I illustrates the overall sequence that was examined as an approach to the synthesis of the natural product isocomene (8).[4,5]

**Scheme I**




Diol 1 was prepared in 88% yield from butyrolactone via a literature process.[6] Initial attempts to convert 1 to 3 involved conversion to 1-(3-chloropropyl)cyclopentene with $CCl_4/PPh_3$, followed by reaction with lithium acetylide–EDA complex in $Me_2SO$. Low yields (<30%) in the first reaction led us to try the procedure shown. Thus 1 (3.22 g) was added to excess $Me_3SiI$ (from 22.88 g of $I_2$ and 9.63 mL of hexamethyldisilane) in $CHCl_3$ (100 mL), yielding 7.95 g (98%) of a mixture of diiodide and iodoalkenes,[7] which was treated directly with lithium acetylide–EDA (5.42 g) in 1:1 THF/$Me_2SO$ (40 mL). Enyne 3 was isolated in 38% yield (1.28 g), together with 5% of its exocyclic olefin isomer.

Treatment of 3 (1.63 g) with $Co_2(CO)_8$ (5.03 g) in $C_6H_6$ (40 mL) yielded enone 5 (0.70 g, 35%), a colorless oil showing IR bands at 1630 and 1690 $cm^{-1}$, and a singlet in the 360-MHz $H^1$ NMR at $\delta$ 5.82. This is therefore the first example of the generation of a quaternary carbon at a multiple ring fusion via this sort of methodology. Addition of 5 (0.12 g) to the reagent prepared from CuI (0.65 g) and MeLi (6.8 mmol) in ether (20 mL) afforded 6 (0.12 g, 90%). Characterization of the latter rests partially on spectroscopic comparisons with the dimethyl derivative prepared by Pirrung[8] (compound 8 in that reference). Both have

(1) Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436.

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(3) Exon, C.; Magnus, P. *J. Am. Chem. Soc.* **1983**, *105*, 2477.

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(6) Canonne, P.; Foscolos, G. B.; Bélanger, D. *J. Org. Chem.* **1980**, *45*, 1828. This route is far superior to approaches involving addition of organometallics to cyclopentenone.

(7) A 3.26:1.00:1.05 mixture of 1-(3-iodopropyl)-1-iodocyclopentane, 1-(3-iodopropyl)cyclopentene, and (3-iodopropylidene)cyclopentane, by 360-MHz NMR.

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