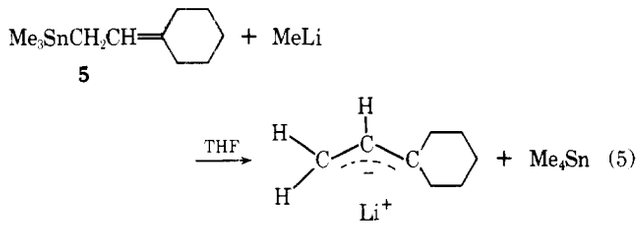
analogue is stable well above its melting point of 163–164.5 °C.

The β-stannyl- and β-silyl-substituted phosphonium halides may be deprotonated to the respective ylides, both of which form deep red-orange solutions in diethyl ether and in tetrahydrofuran. Methyllithium serves well as the base in the case of $[Ph_3PCH_2CH_2SiMe_3]I$ and $[Ph_3PCH(CH_3)CH_2SiMe_3]I$, but for the deprotonation of $[Ph_3PCH_2CH_2SnMe_3]I$, lithium amides, R_2NLi (R = Me_2CH or Me_3Si), must be used, since organolithium reagents do not react regiospecifically, attacking in part at tin as well as at the protons α to phosphorus. The ylides formed, $Ph_3P{=}CHCH_2SnMe_3$, $Ph_3P{=}CHCH_2SiMe_3$, and $Ph_3P{=}C(Me)CH_2SiMe_3$, react readily with aldehydes and, in general, somewhat less well with ketones, to give the expected allylstannanes and allylsilanes (eq 4; Table I).

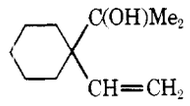
$$Ph_3P{=}CHCH_2MMe_3 + RR'C{=}O \xrightarrow{THF} Me_3MCH_2CH{=}CRR' + Ph_3PO \quad (4)$$

The three allylic tin compounds in Table I undergo ready conversion to the respective allylic lithium reagents, e.g., eq 5. In a typical reaction, **5** (3.74 mmol) in 200 mL of dry THF



5

at 0 °C, under nitrogen, was treated with 4.1 mmol of methyllithium in diethyl ether. The resulting yellow solution was stirred for 30 min at 0 °C and then 20 mmol of acetone was added. After the reaction mixture had been stirred at room temperature for 30 min, hydrolytic workup was followed by GLC analysis of the organic phase to establish the presence of **6** in 89% yield. The results of these experiments are illustrated in Schemes I–III. The product yields are uniformly excellent. A discussion of the observed regioselectivities in the reactions of these ambident reagents will be deferred until this study has been completed.



6

It is obvious that this new route to allylic compounds of silicon and tin should be quite general in its scope of applicability. By appropriate variation of the phosphorus ylide and the carbonyl substrate in these reactions, allylic derivatives of silicon and tin of type $Me_3MCH_2C(R){=}CR'R''$, where R, R′, and R″ should be capable of wide variation, should be accessible. The allyltins thus prepared would provide starting materials for many new allylic lithium reagents. In many cases the direct lithiation procedure, the reaction of RLi/Lewis base or RLi/Me_3COK with an appropriate unsaturated hydrocarbon, would provide the simplest route to the desired allylic lithium reagent.[2] However, the additives which usually are required to effect such metalations may not always be compatible with other functionality in the carbonyl reactant or may interfere in other ways. Also, there will be instances when the appropriate unsaturated hydrocarbon is not available. Thus the versatility of our new procedure and its ease of application may prove very useful in organic and organometallic synthesis.

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Conjugate Addition–Elimination in the Reaction of *B*-1-Alkynyl-9-borabicyclo[3.3.1]nonanes with 4-Methoxy-3-buten-2-one and Related Derivatives. A Convenient New Route to Conjugated Enynones

Summary: *B*-1-Alkynyl-9-borabicyclo[3.3.1]nonanes (*B*-1-alkynyl-9-BBN), easily and quantitatively prepared by the reaction of boron trifluoride diethyl etherate with the corresponding lithium methyl alkynyldialkylborinate,[1] undergo a remarkably facile reaction with the readily available 4-methoxy-3-buten-2-one and related derivatives in hexane at room temperature to provide, in excellent yield, conjugated enynones.

Sir: Recently we described the conjugate addition of *B*-1-alkynyl-9-borabicyclo[3.3.1]nonanes to a variety of α,β-unsaturated ketones, which provided a valuable synthesis of γ,δ-alkynyl ketones.[2] House has suggested that reduction potentials may be used to determine the suitability of substrates toward conjugate addition of organocuprates and perhaps other organometallic reagents.[3] Hooz and Layton, in their work on dialkylalkenyl alanes and dialkylalkynyl alanes, point out that the yields of conjugate addition product appear to correlate well with the reduction potentials of the substrates utilized.[4]

Table I. Conversion of Alkynes into 4-Alkynyl-3-buten-2-ones by the Reaction of the Corresponding *B*-1-Alkynyl-9-BBN Derivatives with 4-Methoxy-3-buten-2-one[a]

Alkyne	Product[b]	Isolated yield, %	Bp, °C (mmHg)	n^{20}D	Mol wt[c] Calcd	Found
1-Hexyne	*trans*-3-Decen-5-yn-2-one	85	86–88 (3.5)	1.5060	150.104	150.102
1-Decyne	*trans*-3-Tetradecen-5-yn-2-one	81	86 (0.001)	1.4922	206.167	206.164
Phenylethyne	*trans*-6-Phenyl-3-hexen-5-yn-2-one	88[d]	45–46[e]		170.073	170.074
3,3-Dimethyl-1-butyne	*trans*-7,7-Dimethyl-3-octen-5-yn-2-one	98[d]	71–72 (3)	1.4898	150.104	150.107
Cyclohexylethyne	*trans*-6-Cyclohexyl-3-hexen-5-yn-2-one	72	54 (0.015)	1.5294	176.120	176.118
5-Chloro-1-pentyne	*trans*-9-Chloro-3-nonen-5-yn-2-one	74	59 (0.015)	1.5296	170.050	170.048
2-Methyl-1-buten-3-yne	*trans*-7-Methyl-3,7-octadien-5-yn-2-one	90[d]	33 (0.016)	1.5488	134.073	134.074

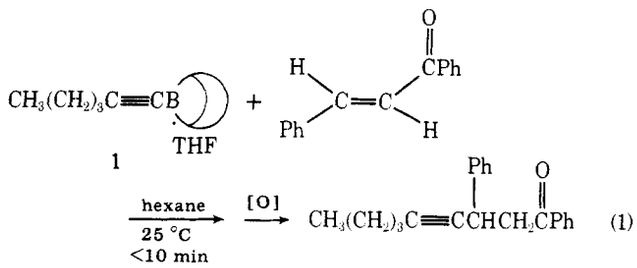
[a] A 20% excess of 4-methoxy-3-buten-2-one was employed in all reactions. [b] Satisfactory IR and ^{1}H NMR were obtained for all compounds. [c] Exact mass was measured on a CEC-21-110 mass spectrometer. [d] Crude yield, >97% pure by GLC analysis. ^{1}H NMR and IR appear identical before and after purification. [e] Melting point.

Table II. Synthesis of Conjugated Enynones by the Addition–Elimination Reaction of *B*-1-*tert*-Butylethynyl-9-BBN with β-Alkoxy α,β-Unsaturated Ketones

Alkoxy enone[a]	Product(s)[b]	Reaction time	% GC yield
(*E*)-4-Methoxy-3-buten-2-one (**5**)	(*E*)-7,7-Dimethyl-3-octen-5-yn-2-one	1 h	100
(*E*)-4,4-Dimethyl-1-methoxy-1-penten-3-one (**6**)	(*E*)-2,2,8,8-Tetramethyl-4-nonen-6-yn-3-one	1 h	100
(*E*)-3-Methoxy-1-phenyl-2-propen-1-one (**7**)	(*E*)-6,6-Dimethyl-1-phenyl-2-hepten-4-yn-1-one	1 h	65
(*E*)-1-Methoxy-2-methyl-1-penten-3-one (**8**)	(*E*)-4,8,8-Trimethyl-4-nonen-6-yn-3-one	4 h	94
4-Methoxy-3-penten-2-one (**9**) (84:16 mixture of *Z*:*E*)[c]	4,7,7-Trimethyl-3-octen-5-yn-2-one (2.1:1 mixture of *E*:*Z*)[c]	2 days	29
(*E*)-4-Methoxy-3-penten-2-one (**10**)[d]	4,7,7-Trimethyl-3-octen-5-yn-2-one (2.7:1 mixture of *E*:*Z*)[c]	2 days	17
3-Ethoxy-2-cyclohexen-1-one (**11**)	3-[3,3-Dimethyl-1-butynyl]-2-cyclohexen-1-one	5 days	0

[a] A 20% excess of alkoxy enone was employed in all reactions. [b] Satisfactory IR, ^{1}H NMR, and exact mass was obtained for all products. [c] Measured by ^{1}H NMR. [d] It is interesting to note that the reaction of this methoxy enone with *B*-1-hexynyl-9-BBN provided a 70% isolated yield of 3-decen-5-yn-2-one after 5 days.

In our studies on the conjugate addition of alkynylboranes, we noted that the addition of *B*-1-hexynyl-9-BBN–THF complex (**1**) to benzalacetophenone was rapid and quantitative, as expected from the increased reduction potential (eq 1).

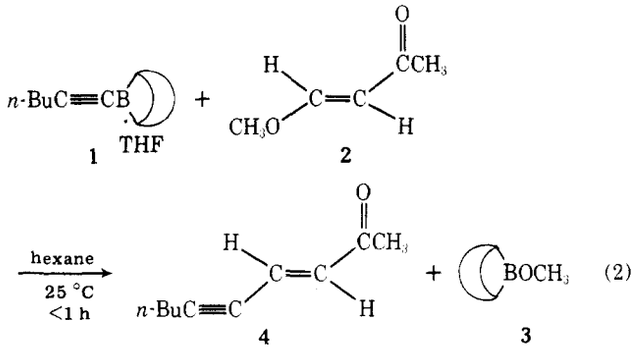


(1)

On the other hand, a β-methoxy substituent lowers the reduction potential, presumably making the substrate less susceptible to conjugate addition. Surprisingly, the reaction of **1** with 4-methoxy-3-buten-2-one (**2**) proved to be exceedingly rapid, complete in <1 h at 25 °C. Moreover, the conjugate addition was accompanied by the facile elimination of *B*-methoxy-9-BBN (**3**), providing the corresponding *trans*-4-alkynyl-3-buten-2-one (**4**) in nearly quantitative yield (eq 2). This appeared to be an exceptionally promising synthesis of conjugated enynones. Consequently, we undertook to explore this discovery.

Only two routes to 4-alkynyl-3-buten-2-ones have been described.[5,6] Both methods require preparation of several intermediates and provide only moderate yields of product. Neither has been demonstrated to be general for a variety of alkynes.

In view of these limitations, we undertook to explore the generality of the new procedure, utilizing a representative variety of *B*-1-alkynyl-9-BBN compounds. Indeed, this study



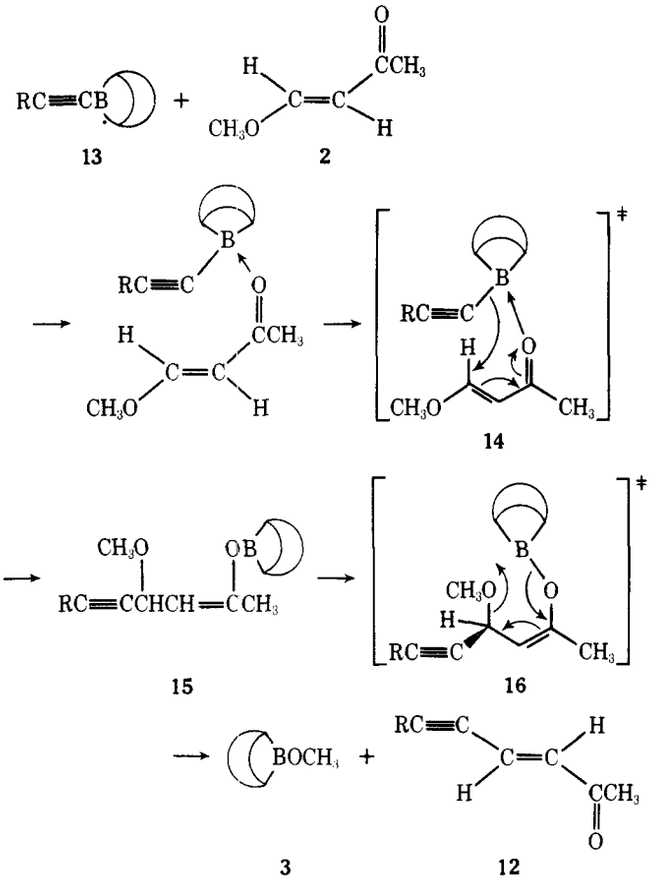
(2)

revealed that this synthesis proceeds with remarkable ease with a wide variety of alkynylboranes (Table I).

We utilized *B*-1-*tert*-butylethynyl-9-BBN in a brief exploration of this reaction with other β-methoxy α,β-unsaturated ketones. Ketones capable of assuming a cisoid conformation (**5–10**) reacted satisfactorily to give products in the indicated yields. On the other hand, that derivative not capable of assuming such a cisoid conformation (**11**) gave no indication of reaction in the desired manner (Table II).

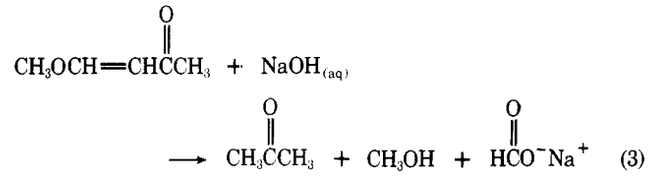
Proton NMR experiments confirm that the 4-alkynyl-3-buten-2-one (**12**) and *B*-methoxy-9-BBN (**3**) are produced spontaneously in the reaction mixture and are not a result of the workup conditions. These results are consistent with a process that involves an initial coordination of the carbonyl group at the ketone **2** with the boron atom of the 9-BBN derivative **13**, followed by the formation of a cyclic transition state, **14**, giving the intermediate **15**, which rapidly eliminates *B*-methoxy-9-BBN (**3**) through another cyclic transition state **16**, yielding the desired product **12** (Scheme I). In all but one case, the reaction is stereospecific, producing only the *E* isomers, as indicated by GLC analysis, ^{13}C NMR, ^{1}H NMR (J_{vinyl}

Scheme I



= 16 Hz), and IR (960–965 cm^{-1}) spectra.

The simple work-up procedure for this reaction provides highly pure products (≥97%) without the need for further purification of the crude material. The small excess of 4-methoxy-3-buten-2-one utilized in the reaction is conveniently hydrolyzed under the basic workup conditions to by-products which are water soluble and/or highly volatile and therefore can be readily removed from the desired products (eq 3).[7]



(3)

Likewise, the *B*-methoxy-9-BBN by-product is converted by the standard peroxide oxidation[8] into water-soluble *cis*-1,5-cyclooctanediol and boric acid, providing clean products after simple extraction of the reaction mixture.

The following procedure for the preparation of *trans*-7,7-dimethyl-3-octen-5-yn-2-one is representative. To 7.44 g (27.1 mmol) of 3,3-dimethyl-*B*-1-butynyl-9-BBN–THF complex,[1] in an oven-dried nitrogen-flushed 100-mL flask equipped with a magnetic stirring bar, a septum inlet, and a gas inlet tube with stopcock, was added 40 mL of dry hexane. To the solution was added 3.26 g (32.6 mmol) of 4-methoxy-3-buten-2-one[9] and the reaction mixture was stirred for 1 h at 25 °C to ensure complete reaction. Oxidation was accomplished by the rapid addition of 12 mL of 3 M NaOH, followed by dropwise addition of 12 mL of 30% H_2O_2 (*Caution:* exothermic!). After stirring at 25 °C for 2 h, the reaction mixture was poured into a separatory funnel and the layers were separated. The aqueous layer was washed with pentane (three 15-mL portions) and the combined organic extracts were washed with a 1:1 H_2O–THF solution (three 30-mL portions). The organic phase was dried over anhydrous $MgSO_4$ and filtered, and the volatiles were removed in vacuo to provide 3.99 g (98%) of *trans*-7,7-dimethyl-3-octen-5-yn-2-one, 97% pure by GLC analysis: $n^{20}D$ 1.4898; IR (neat) 2230, 1670, 1595, 960 cm^{-1}; ^1H NMR (CCl_4, Me_4Si) δ 1.23 (s, 9 H), 2.18 (s, 3 H), 6.22 (d, 1 H, J = 16 Hz), 6.58 (d, 1 H, J = 16 Hz). Distillation, bp 71–72 °C (3 mmHg), provided analytically pure material.

It is evident that this procedure makes it practical to synthesize highly functionalized, stereospecific products in high yields that should be useful in organic synthesis. Furthermore, this development makes available an exciting new reaction of organoboranes, and research is underway to examine its full potential.

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