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ORGANIC SYNTHESIS USING 1-METHOXY-1,2,3-BUTATRIENYLBORATES. II. A FACILE SYNTHESIS OF 2,5-DIALKYL-3-METHYLFURANS FROM 1,4-DIMETHOXY-2-BUTYNE, B-ALKYLCATECHOLBORANES AND ALDEHYDES

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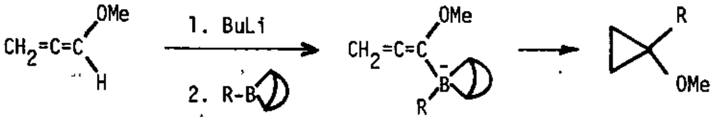
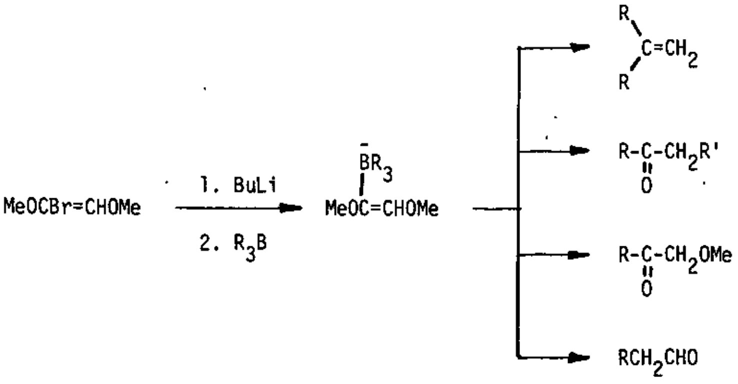
Abstract — 2,5-Dialkyl-3-methylfurans are obtained in excellent yields by the reaction of acetic acid with 1-methoxy-1,2,3-butatrienylborates prepared from 1-methoxy-1,2,3-butatrienyllithium and B-alkylcatecholboranes, followed by treatment with aldehydes.

Recently we have reported on the organic synthesis using special borates in which borate boron atoms and methoxy groups combine with the same carbon-carbon double bond carbon. For example, the reaction of acetic acid with ate-complexes formed from B-alkyl-9-borabicyclo[3,3,1]nonanes (B-alkyl-9-BBN) and 1-lithio-1-methoxyallene gave the corresponding 1-alkyl-1-methoxycyclopropanes in good yields (eq. 1).[1] 1,2-Dimethoxyethenyltrialkylborates readily obtainable from organoboranes were found to be used as effective intermediates for syntheses of 1,1-dialkylethenes (eq. 2),[2] ketones (eq. 3),[3] 1-methoxy-2-alkanones (eq. 4),[4] and aldehydes (eq. 5).[5]



(1)



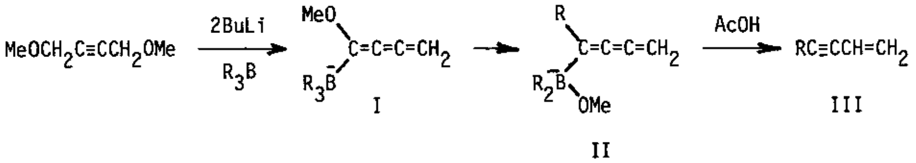
(2)

(3)

(4)

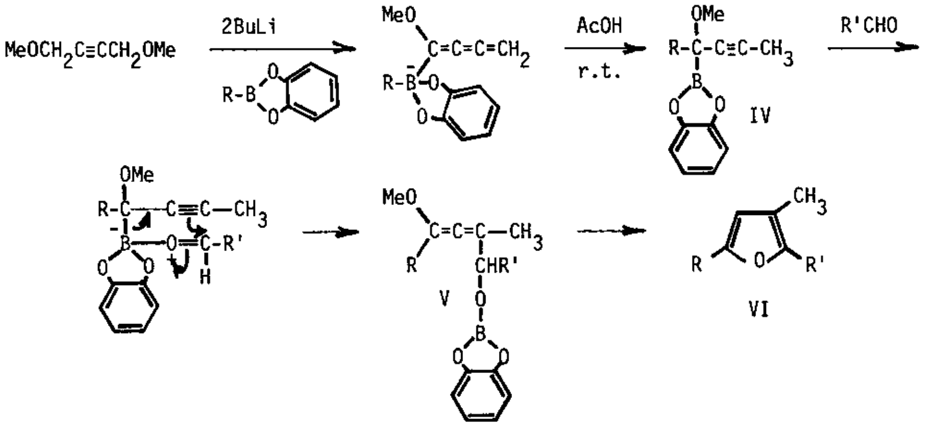
(5)

Most recently, it was reported that 1-alken-3-ynes (III) were readily prepared by the reaction of 1-methoxy-1,2,3-butatrienyllithium and trialkylboranes, followed by protonolysis with acetic acid (eq. 6).[6] As shown in eq. 6, this reaction is considered to proceed through alkyl group migration



(6)

from boron to the adjacent carbon with elimination of methoxy group, and the sequent protonation at the γ-carbon with respect to the boron atom. Thereafter, we inadvertently discovered that when B-alkylcatecholboranes are employed, instead of trialkylboranes, the alkyl migration occurs only by addition of acetic acid without elimination of methoxy group, and the protonation takes place at the δ-carbon to give the intermediates (IV) which are stable at room temperature (eq. 7). Such



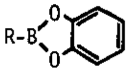
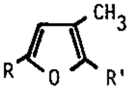
(7)

intermediates seem to have a possibility to be converted by the reaction with aldehydes into the corresponding allenic alcohol derivatives (V) which are good precursors to 2,5-dialkyl-3-methylfurans (VI).[7-9] In this paper, we wish to report that as expected, the reaction proceeds smoothly to yield such trialkylfurans in excellent yields.

The following procedure for the preparation of 5-hexyl-2,3-dimethylfuran is typical. n-Butyllithium (2.86 ml of a 1.79 M solution in hexane, 5.13 mmol) was slowly added to a solution of 1,4-dimethoxy-2-butyne (293 mg, 2.56 mmol) in 10 ml of dry ether under nitrogen atmosphere at -78 °C. Under stirring for 10 min at -78 °C and for 20 min at -45 °C, B-hexylcatecholborane (351 mg, 1.72 mmol) was added to the pale yellow suspension, and the mixture thus obtained was stirred for 30 min. The reaction mixture was treated with acetic acid (0.4 ml, 6.9 mmol) at the same temperature for 10 min with stirring, and was then allowed to warm to room temperature. After 1 h, acetaldehyde

(53 mg, 1.20 mmol) was added to the solution at 0 °C, and the mixture was stirred for 12 h. Finally, 6 ml of 1 M aqueous solution of sodium hydroxide was added, and the organic layer separated was analyzed by glpc. The analysis showed that 1.18 mmol of 5-hexyl-2,3-dimethylfuran (98% yield) had been formed. The representative results are summarized in Table 1.

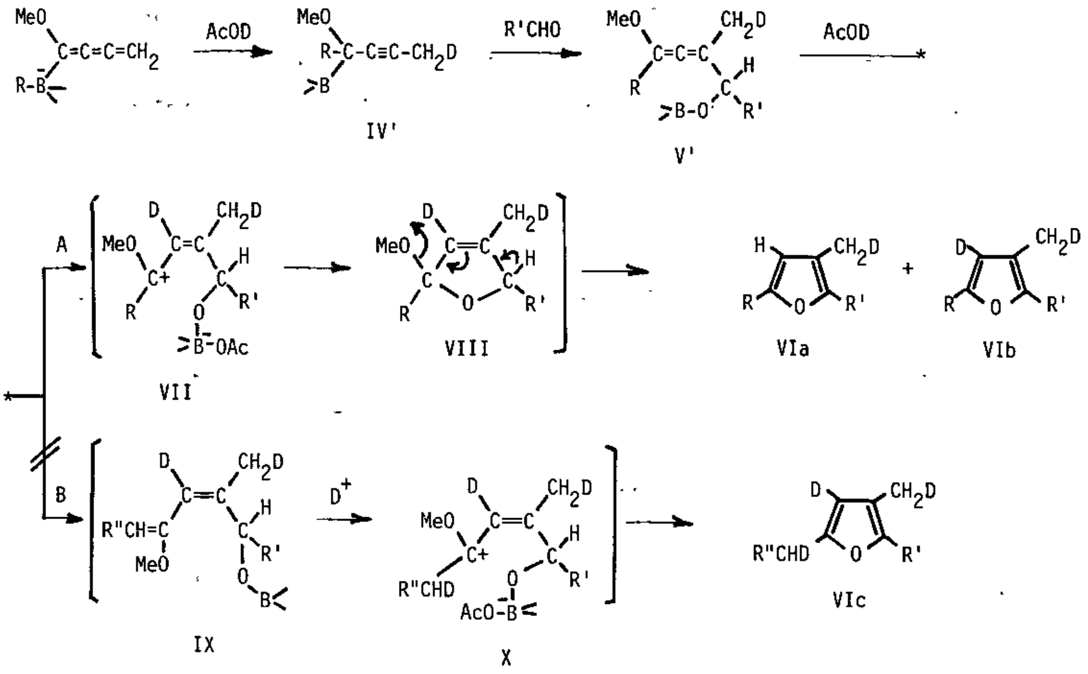
Table 1. Synthesis of 2,5-Dialkyl-3-methylfurans

	Aldehyde (R'CHO), R'	Yield of , %[a]
Hexyl	Methyl	98
"	Ethyl	98
"	Phenyl	96
"	Vinyl	88[b]
Heptyl	Ethyl	97
"	Phenyl	97
"	Vinyl	83[b]

[a] Glpc yield based on the aldehyde used.

[b] Commercial acrolein (purity, 90%) was employed without purification. No formation of 1,4-adducts was observed.

The reaction appears to proceed through the following pathways (Path A). Normant et al.[7] reported the same type of furan synthesis from 4-methoxyalka-2,3-dien-1-ols (V', >B=H), for which they proposed the mechanism through the intermediates (IX, >B=H), as depicted in Scheme 1. If such a reaction occurs by the reaction mechanism, the deutero-furan derivatives (VIc) may be obtained by the protonolysis with deutero-acetic acid. However, the products actually observed were not them, but deutero-furans (VIa and VIb). For example, when acetic acid-d_1 (6 equivalents) was used as a protonolysis agent for the allenylic borate (V'; R=hexyl, R'=methyl) prepared from 1-methoxy-1,2,3-butatrienyllithium, B-hexylcatecholborane, and acetaldehyde, 5-hexyl-3-deuteromethyl-2-methylfuran (VIa; R=hexyl, R'=methyl) and 5-hexyl-4-deutero-3-deuteromethyl-2-methylfuran (VIb; R=hexyl, R'=methyl) were obtained in a ratio of 10:90 without accompanying the deutero-furan derivative (VIc). The formation of VIa is elucidated by protonolysis with the usual acetic acid produced by scrambling between acetic acid-d_1 and the mathanol yielded from the intermediate (VIII). Such evidence supports the reaction mechanism through the path A in Scheme 1.



Scheme 1

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