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THE REACTION OF LITHIUM TRIALKYL(1-ALKYNYL)BORATES WITH ORTHOESTERS IN THE PRESENCE OF TITANIUM TETRACHLORIDE. A NEW SYNTHESIS OF α,β-UNSATURATED CARBONYL COMPOUNDS

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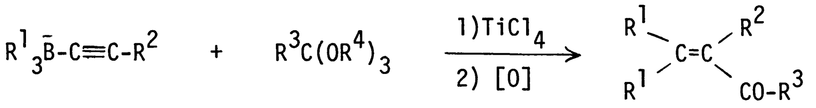
Trialkyl(1-alkynyl)borates readily available from trialkylboranes and lithium acetylides react with orthoesters in the presence of titanium tetrachloride, followed by the oxidation with hydrogen peroxide and sodium hydroxide to give the corresponding α,β-unsaturated carbonyl compounds.

Although the potential significance of 1-alkynylborates in organic synthesis has been recognized in the reactions with electrophiles such as proton, halogens, and alkyl halides,1) the synthetic usefulness is limited because of their low reactivity to the electrophiles such as ketones, aldehydes, and esters.2) Recently, we have found that methyl vinyl ketone can be used in the reaction of 1-alkynylborates by the activation with titanium tetrachloride.3) We wish to report here that orthoesters can also react with 1-alkynylborates in the presence of titanium chloride followed by the usual alkaline hydrogen peroxide oxidation to give α,β-unsaturated aldehydes or ketones (Eq. 1).

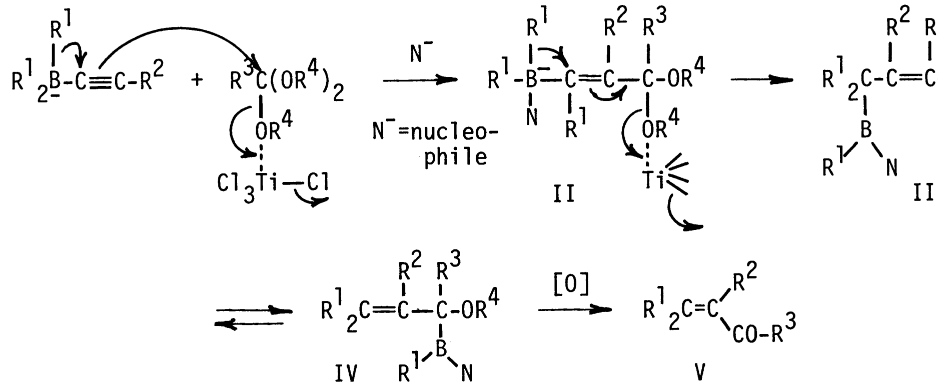


$$R^1_3\bar{B}\text{-}C{\equiv}C\text{-}R^2 \quad + \quad R^3C(OR^4)_3 \quad \xrightarrow[2)\ [O]]{1)\,TiCl_4} \quad (R^1)_2C{=}C(R^2)CO\text{-}R^3 \qquad (1)$$

A typical procedure is as follows. Treatment of phenylethyne (306 mg, 3 mmol) in 5 ml of anhydrous THF with butyllithium in ether (2 ml of a 1.5 M solution, 3 mmol) at 0 °C gave the corresponding lithium acetylide. After stirring for 30 min at the temperature, tributylborane in THF (2 ml of a 1.5 M solution, 3 mmol) was added to prepare the alkynylborate. The reaction mixture was stirred for 30 min at 0 °C, and then cooled to -78 °C. Triethyl orthoformate (740 mg, 5 mmol) and titanium tetrachloride in dichloromethane (2.5 ml of a 2 M solution, 5 mmol) were added successively. The resulting dark brown solution was stirred at -78 °C for 2 h and at room temperature overnight. Finally the reaction mixture was oxidized with 3 ml of 3 M aq. NaOH and 3 ml of 30% aq. hydrogen peroxide. Analysis of the organic layer by glpc indicated that 2-phenyl-3-butyl-2-heptenal had been formed in quantitative yield. The representative results are shown in Table 1 (entry 1-5).

Although other orthoformates were also examined in the reaction of tributyl(phenylethynyl) borate, the highest yield of 2-phenyl-3-butyl-2-heptenal (I) was obtained by using triethyl orthoformate. The results are as follows: $CH(OMe)_3$ (yield of the aldehyde (I)=49%), $CH(OPr\text{-}i)_3$ (94%), and $CH(OBu)_3$ (67%). The reaction can be extended to trialkyl orthoacetates and orthopropionates, and the expected unsaturated ketones can be obtained (entry 6-11 in Table 1).

The reaction is considered to proceed through the following reaction path (Eq. 2).4) An orthoester activated with $TiCl_4$ reacts with a lithium trialkyl(1-alkynyl)borate with the migration of alkyl group from boron to carbon to give the intermediate (II), which is then converted into III. The allylic borane (III) is isomerized to IV, which is finally oxidized to give the unsaturated carbonyl compound (V).



(2)

Table 1. Synthesis of α,β-Unsaturated Aldehydes and Ketones.

Entry	R^1, R^1_3B	$R^2C{\equiv}CH$	$R^3C(OR^4)_3$	Product[a)]	Yield,[b)] %
1	Propyl	Phenylethyne	$HC(OEt)_3$	$Pr_2C{=}C(Ph)CHO$[c]	82
2	Butyl			$Bu_2C{=}C(Ph)CHO$[c]	100
3	Isobutyl			$i\text{-}Bu_2C{=}C(Ph)CHO$[c]	82
4	Hexyl			$Hex_2C{=}C(Ph)CHO$[c]	55
5	Butyl	1-Hexyne		$Bu_2C{=}C(Hex)CHO$[c]	33
6	Butyl	Phenylethyne	$MeC(OMe)_3$	$Bu_2C{=}C(Ph)COMe$	65
7	Propyl		$MeC(OEt)_3$	$Pr_2C{=}C(Ph)COMe$	40
8	Butyl		$EtC(OEt)_3$	$Bu_2C{=}C(Ph)COEt$	51
9	Propyl			$Pr_2C{=}C(Ph)COEt$	55
10	Butyl	1-Hexyne	$MeC(OMe)_3$	$Bu_2C{=}C(Hex)COMe$	50
11	Isobutyl			$i\text{-}Bu_2C{=}C(Hex)COMe$	40

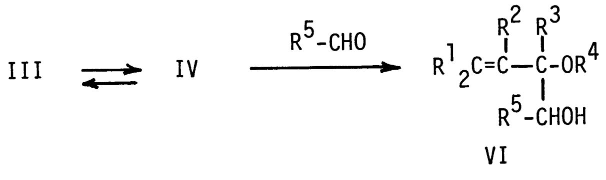
a. All products were identified by NMR, MS. and IR spectra.

b. Glpc yield based on the organoborane used.

c. Products are not stable in air and decompose gradually.

References

1) a) A. Pelter and K. Smith, in "Comprehensive Organic Chemistry," edited by D. N. Jones, Pergamon, Oxford (1979), Vol. 3, P. 883. b) A. Suzuki, Accts. Chem. Res., 15, 178 (1982). 2) E. Negishi, J. Organometal. Chem., 108, 281 (1976). 3) S. Hara, K. Kishimura, and A. Suzuki, Chemistry Lett., 1980, 221, and recently Pelter et al. have reported that 1,1-difunctional ethylenes such as alkylidenemalonates and alkylideneacetoacetates can react with alkynylborates without catalysts via the Michael-type addition fashion. A. Pelter and J. M. Rao, Tetrahedron Lett., 22, 797 (1981). 4) When an aldehyde was added to the reaction mixture, instead of the oxidation, the adduct (VI) was obtained. Consequently, the allylic borane derivative (III) or (IV) seems to be present as the reaction intermediate.



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