CHEMISTRY LETTERS, pp. 999-1002, 1977. Published by the Chemical Society of Japan

FACILE ELECTROCHEMICAL ALKYLATION OF 1-ALKYNES WITH ORGANOBORANES

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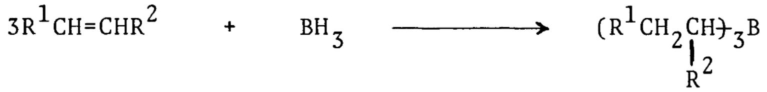
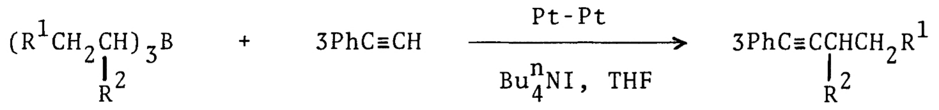
Trialkylboranes are readily electrolyzed in an undivided cell by using two platinum plates as the electrodes in the presence of 1-alkynes in a tetrahydrofuran solution containing tetraalkylammonium halide to give corresponding alkynes in good yields. In the case of phenylacetylene, all alkyl groups of trialkylboranes are used for alkylation of the alkyne.

We have previously reported that electrochemical reactions of trialkylboranes with substrates containing acidic hydrogens such as acetonitrile,[1] nitromethane,[2] and piperidines[3] proceed smoothly to provide convenient routes to nitriles, nitroalkanes, and N-alkylpiperidines, respectively, in good yields. On the other hand, we have also reported that the reactions of iodine with the ate-complexes prepared from trialkylboranes and lithium acetylides give corresponding alkynes in good yields.[4] It was shown that this procedure provides a new simple, general synthesis of alkynes with its exceptionally broad range of applicability since it readily permitted the introduction of secondary and aryl groups as easily as primary groups, in contrast to conventional methods using nucleophilic substitution reactions of alkali metal acetylides.[5] However, there was a disadvantage that in the reaction only one alkyl group of trialkylborane is utilizable.

In an attempt to overcome this difficulty, we examined the electrochemical reactions of trialkylboranes with phenylacetylene, and found that trialkylboranes are readily electrolyzed between two platinum electrodes in the presence of phenylacetylene in a tetrahydrofuran solution containing tetra-n-butylammonium iodide as a supporting electrolyte to produce corresponding 1-alkyl-2-phenylacetylenes in high yields (eqs. 1 and 2). The reaction was carried out by means of controlled current electrolysis in an undivided cell. The results of representative reactions are summarized in Table 1. It appears that all alkyl groups of trialkylboranes undergo the electrochemical alkylation to give corresponding phenylalkynes, and there is no difficulty in introducing secondary alkyl groups as well as primary alkyl groups. Instead of phenylacetylene, alkylacetylene was also found to be useful as a substrate in this type of electrochemical reaction, but in this case only an alkyl group of trialkylborane was employed. For example, electrolysis of 1-hexyne in the presence of tri-n-butylborane or tri-sec-butylborane under the same reaction conditions gave 5-decyne in an 85% yield or 3-methyl-4-nonyne in an 87% yield, based on the organoborane used.



$$3R^1CH{=}CHR^2 \quad + \quad BH_3 \longrightarrow (R^1CH_2\underset{R^2}{CH})_3B \qquad (1)$$



$$(R^1CH_2\underset{R^2}{CH})_3B \quad + \quad 3PhC{\equiv}CH \xrightarrow[Bu^n_4NI,\ THF]{Pt\text{-}Pt} 3PhC{\equiv}C\underset{R^2}{CH}CH_2R^1 \qquad (2)$$

Table 1. Electrochemical Reaction of Trialkylboranes with Phenylacetylene in THF Solution Containing Tetra-n-butylammonium Iodide[a]

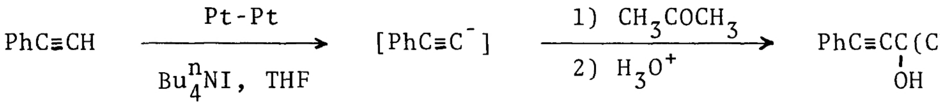
Olefin used to form organoborane	R^1	R^2	Product[b]	Yield[c] (%)
1-Pentene	C_3H_7	H	1-Phenyl-1-heptyne	75
1-Butene	C_2H_5	H	1-Phenyl-1-hexyne	83
Propene	CH_3	H	1-Phenyl-1-pentyne	94
2-Butene	CH_3	CH_3	1-Phenyl-2-methyl-1-pentyne	91
Cyclopentene	$-(CH_2)_3-$		Cyclopentylphenylacetylene	70

a) The reaction was carried out under the conditions described in the preparation for 1-phenyl-1-pentyne from tri-n-propylborane.

b) All products were either compared with authentic samples or were found to exhibit analytical data and spectra in accordance with the assigned structures.

c) Analyzed by glpc, based on olefin employed.

Although the reaction mechanism is not clear at present, several points must be noted. First, tetra-n-butylammonium iodide was found to be effective as the supporting electrolyte, whereas the electrolysis using tetra-n-butylammonium perchlorate as the electrolyte produced no detectable amount of the corresponding alkyne. Consequently, the halide ions seem to play an important role in this reaction. Second, no reaction occurred when the electrolysis was carried out in a divided cell. This fact suggests that the present synthesis requires coupled chemical reactions at the anode and cathode.[1,2] Third, the formation of acetylide anion, $\mathrm{PhC{\equiv}C^-}$, at the cathode is supported by the following evidence. When a mixture of phenylacetylene and acetone in a tetrahydrofuran solution containing tetra-n-butylammonium iodide was electrolyzed under the same conditions, 1-phenyl-3-hydroxy-3-methyl-1-butyne was obtained (eq. 3). This may be explained as a nucleophilic attack of initially formed acetylide anion to acetone. A similar type of the reaction mechanism was recently reported in the cathodic reaction of phenylacetylene with alkyl halides in a HMPA solution containing tetra-n-butylammonium iodide.[6]



$$\mathrm{PhC{\equiv}CH} \xrightarrow[\mathrm{Bu^n_4NI,\ THF}]{\mathrm{Pt\text{-}Pt}} [\mathrm{PhC{\equiv}C^-}] \xrightarrow[\mathrm{2)\ H_3O^+}]{\mathrm{1)\ CH_3COCH_3}} \mathrm{PhC{\equiv}C}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{(CH_3)_2} \qquad (3)$$

The following procedure is representative. The electrolysis is carried out in the usual undivided cell equipped with two platinum plate electrodes ($2.0 \times 2.0\ \mathrm{cm^2}$), a magnetic stirring bar, and a reflux condenser. Tri-n-propylborane (1.2 mmol, 1 ml of 1.2 M solution of the organoborane prepared by hydroboration in advance), phenylacetylene (4.5 mmol, 0.46 g), and tetra-n-butylammonium iodide (2.7 mmol, 1.0g) are dissolved in 40 ml of tetrahydrofuran. The solution is electrolyzed at a constant current ($25\ \mathrm{mA/cm^2}$) for 2 h at 45°C under a nitrogen atmosphere. Then, the reaction mixture is oxidized by adding 2.0 ml of 3N aqueous sodium hydroxide and 2.0 ml of 30% hydrogen peroxide for 2 h at room temperature. The organic layer is separated and then dried over magnesium sulfate. Analysis of the organic layer by glpc indicated that 3.4 mmol (94%) of 1-phenyl-1-pentyne had been formed: n_D^{20} 1.5387; nmr(δ in $\mathrm{CCl_4}$), 1.08 (t, 3H), 1.63 (sextet, 2H), 2.38 (t, 2H), 7.25 (m, 5H); ir(neat), ν_{max} 2230 $\mathrm{cm^{-1}}$ ($\mathrm{-C{\equiv}C-}$); mass, m/e 144 ($\mathrm{M^+}$).

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(Received June 15, 1977)