

A CONVENIENT STEREOSPECIFIC ALKYLATION OF PHENYLACETYLENE BY
ELECTROCHEMICAL REACTION OF ORGANOBORANES

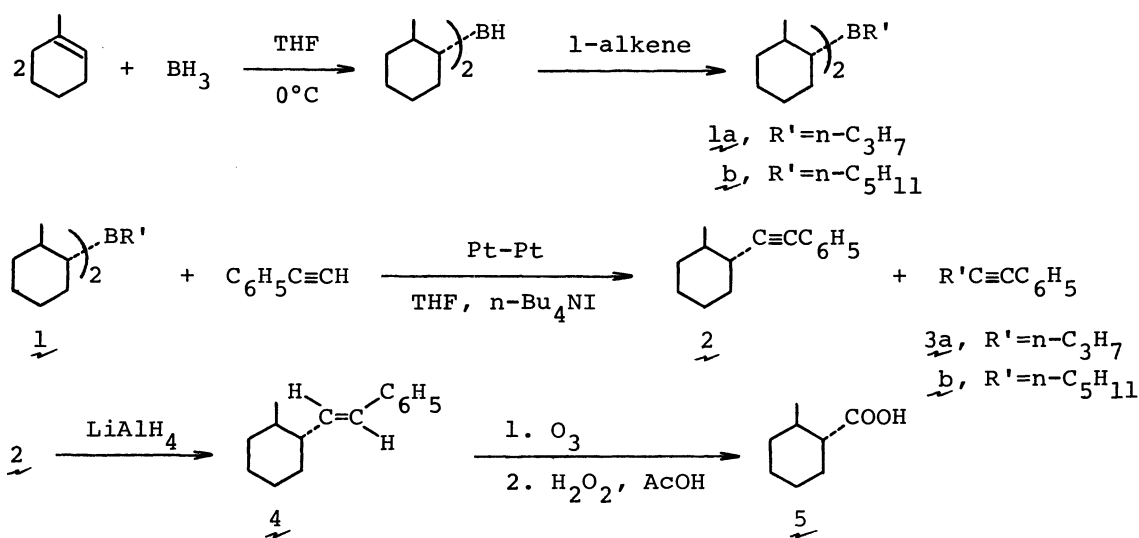
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The electrochemical reaction of phenylacetylene with trialkylboranes in a tetrahydrofuran solution containing tetraalkylammonium halide gives the corresponding alkynes via a retention of configuration with respect to the boron-carbon bonds. The reaction mechanism is also discussed.

We have previously reported that the reaction of iodine with ate-complexes prepared from trialkylboranes and lithium acetylides gives corresponding internal alkynes in good yields,¹ and also reported that the electrochemical reaction of 1-alkynes with trialkylboranes similarly gives corresponding alkynes in excellent yields under mild conditions.² Such procedures have been shown to provide new simple, general syntheses of alkynes with a broad range of applicability since they readily permit the introduction of secondary alkyl and aryl groups as easily as primary alkyl groups. In the electrochemical procedure² there is an additional advantage that all alkyl groups of trialkylboranes are used as alkylating agents. We wish to report here that the electrochemical alkylation of phenylacetylene proceeds via a complete retention of the configuration of the boron-carbon bond.

Hydroboration of 1-methylcyclohexene at 0°C followed by further reaction with propene or 1-pentene smoothly gives bis(trans-2-methylcyclohexyl)propyl- (1a) or bis(trans-2-methylcyclohexyl)pentylborane (1b) [Scheme 1].^{3,4} Electrochemical

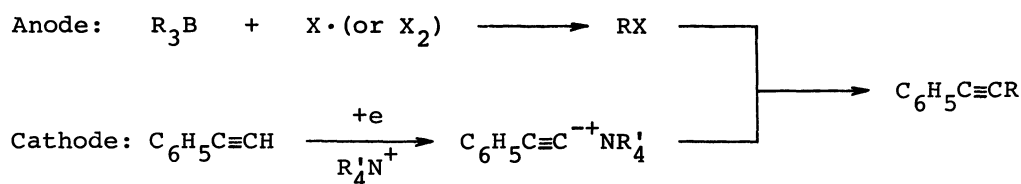


Scheme 1

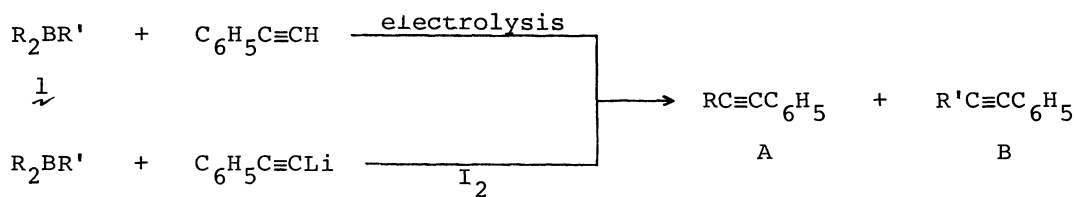
reaction of 1a with phenylacetylene in a tetrahydrofuran solution containing tetra-n-butylammonium iodide as a supporting electrolyte produced 1-(trans-2-methylcyclohexyl)-2-phenylethyne (2) [n_D^{20} 1.5059; NMR (CCl_4) δ 1.12 (d, 3H, $J=5.7$ Hz), 0.8-2.3 (m, 10H), 7.26 ppm (m, 5H); m/e (rel. intensity) 196 (M^+ , 100), 185 (31), 171 (43), 157 (70), 143 (77), 130 (89), 117 (65%)]⁵ and 1-phenyl-1-pentyne (3a)^{2,5} in good yields [Scheme 1]. Stereochemistry of 2 was confirmed by the following evidence. Reduction⁶ of a tetrahydrofuran solution of 2 with lithium aluminum hydride gave (E)-1-(trans-2-methylcyclohexyl)-2-phenylethylene (4)⁵ in a 63% yield. Ozonolysis of a methanol solution of 4 followed by treatment with 15% hydrogen peroxide and acetic acid gave benzoic acid and trans-2-methylcyclohexanecarboxylic acid (5). Retention time of 5 on glpc analysis and the NMR spectrum were completely identical with those of the authentic sample prepared by the base-catalyzed isomerization of cis-2-methylcyclohexanecarboxylic acid, which was obtained by hydrogenation of an acetic acid solution of o-toluic acid over platinum oxide.⁷ Glpc analysis of the electrolysis product showed only two peaks due to 2 and 3a and glpc of cyclohexanecarboxylic acid derived from 2 gives only the peak of 5. Accordingly, the electrochemical alkylation was found to produce the corresponding alkynes with a complete retention of the configuration with respect to the boron-carbon bond. Similar electrochemical reaction of 1b with phenylacetylene was also shown to undergo stereospecifically to give 2 and 3b^{2,5} in good yields. Furthermore, the stereochemistry of the reaction of iodine with the ate-complex formed from 1 and lithium phenylacetylide was also examined, and it was indicated that the reaction also proceeds through a complete retention, as reported before.⁸ Representative results are summarized in Table 1.




Hydroboration of 1-methylcyclohexene with borane at 65°C followed by refluxing in THF for 10 h gave a mixture of several trialkylboranes, which were converted into trans-2-methylcyclohexanol (70%), 3-methylcyclohexanol (25%) and cyclohexylmethanol (5%) upon oxidation with alkaline hydrogen peroxide. Electrolysis of the organoborane mixture in the presence of phenylacetylene under the conditions mentioned above produced the corresponding alkynes 2 (68%), 1-(3-methylcyclohexyl)-2-phenylethyne (24%) and 1-cyclohexylmethyl-2-phenylethyne (8%). This result shows that the electrochemical alkylation proceeds regioselectively.

We have proposed that the electrochemical alkylation of 1-alkynes goes on via nucleophilic attack of acetylide anion formed at a cathode to alkyl halide formed at an anode [Scheme 2].² However, the stereospecificity and regioselectivity of the present electrochemical alkylation suggest different reaction pathways from those mentioned in Scheme 2. The bromide isolated from an anodic oxidation of 1a in a tetrahydrofuran solution containing tetra-n-butylammonium bromide using a



Scheme 2

Table 1. Electrochemical Reaction of Phenylacetylene with R_2BR' and the Reaction of Iodine with Lithium 1-Alkynyltriorganoborates from R_2BR' 

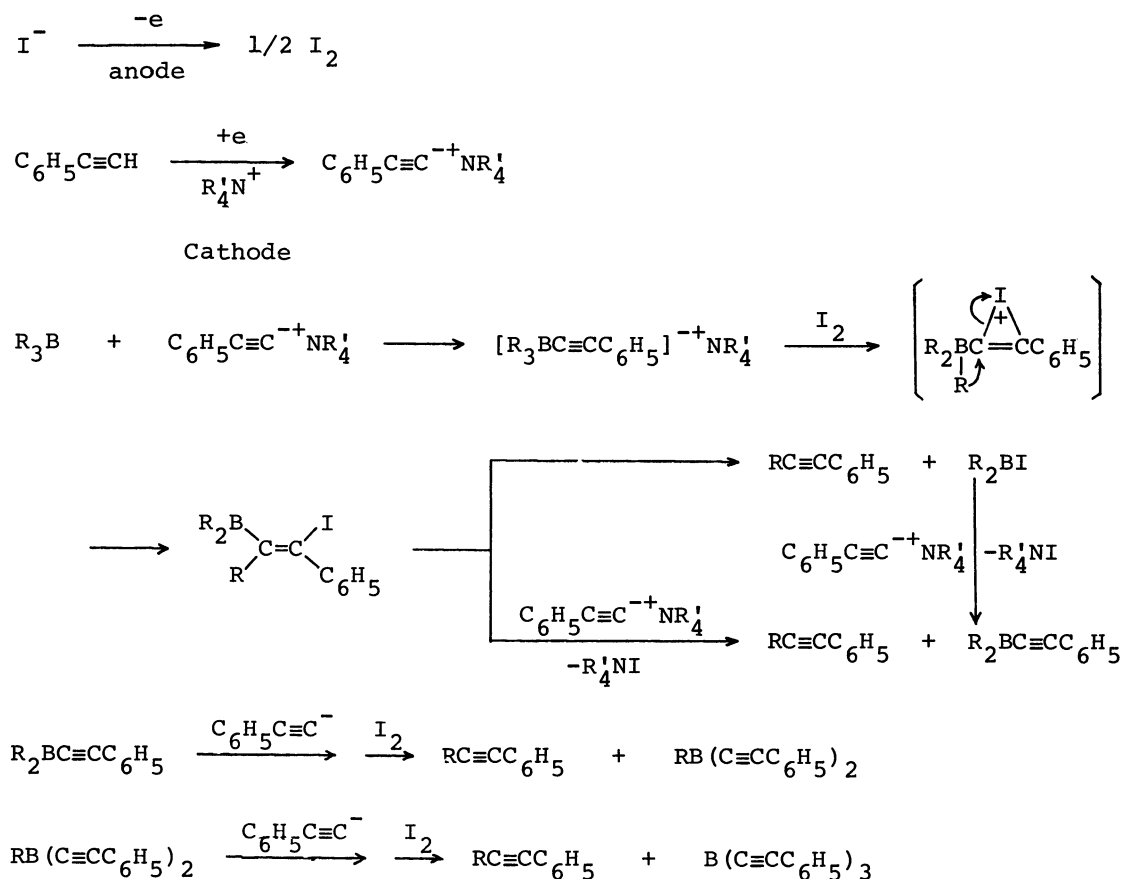
Organoborane		Yield ^a of Product (%)			
		Electrolysis ^b		Reaction with I_2 ^c	
		A	B	A	B
	$n-C_3H_7$ (<u>1a</u>)	162	79	49	42
	$n-C_5H_{11}$ (<u>1b</u>)	128	70	44	39
	$n-C_3H_7$	90	76	32	67

a) Analyzed by glpc, based on organoborane employed.

b) Organoborane (1, 1 mmol), phenylacetylene (9 mmol) and tetra-*n*-butylammonium iodide (2.7 mmol) dissolved in 40 ml of THF was electrolyzed at a constant current (33 mA/cm²) for 3.5 h at 45°C under a nitrogen atmosphere. The electrolyzed mixture was oxidized with alkaline hydrogen peroxide.

c) The reaction was carried out by the method described in ref. 1.

divided cell was not cis-2-methylcyclohexyl bromide (c-6) alone, but a mixture of c-6 (27%), trans-2-methylcyclohexyl bromide (t-6, 21%) and 3-methylcyclohexyl bromide (7, 52%).⁵ Alkynes which might be formed by nucleophilic substitution of the latter two bromides t-6 and 7 were not entirely obtained in the present electrochemical reaction of 1a with phenylacetylene. Furthermore, it has been found² that no reaction occurs when the electrolysis is carried out in a divided cell, the halide ion of a supporting electrolyte plays an important role in the reaction, and the acetylide anion was actually formed at a cathode.⁹ Judging from these results, we now propose the following mechanism [Scheme 3]. Anodic oxidation of iodide ion of a supporting electrolyte gives iodine.¹⁰ On the other hand, trialkylboranes react with acetylides formed at a cathode to give corresponding 1-alkynyltrialkylborates. Such complexes react with iodine to induce transfer of an alkyl group from boron to carbon. Chemical reaction of iodine with 1-alkynyltriorganoborate stops at a transfer of one alkyl group.¹ However, in the present electrochemical reaction, acetylide ions are continuously generated at a cathode, and these anions may produce $R_2BC\equiv CC_6H_5$ and $RB(C\equiv CC_6H_5)_2$, which result in the transfer of the second and the third alkyl groups.



Scheme 3

References

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4. Stereochemistry of 1 was confirmed from the results that the oxidation of 1 with alkaline hydrogen peroxide produced only trans-2-methylcyclohexanol.
5. All products were either compared with authentic samples or were found to exhibit analytical data and spectra in accordance with the assigned structures.
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