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LETTERS

ELECTROCHEMICAL ALKYL TRANSFER REACTIONS OF TRIALKYLBORANE TO CARBONYL COMPOUNDS BY USE OF COPPER SACRIFICIAL ANODE

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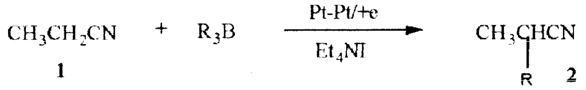
Abstract: Alkyl groups in trialkylboranes were successfully transferred to carbonyl compounds in the presence of the platinum cathode and copper anode by electrochemical method. The new, mild electrochemical alkyl transfer reaction produced various substituted alcohols in good yields.

Many structurally diversed trialkylboranes, readily available from the parent alkenes *via* hydroborations[1], have been effectively used for various synthetic transformations. For nucleophilic alkyl transfer reactions to carbonyl groups, however, only a few trialkylboranes were reported; they are tris(2-methylallyl)borane[2], α-(3-trimethylsilyl)allyldialkoxyboranes[3] and α-trimethyl-9-crotyl-9-BBN[4]. In an attempt to expand the scope in application, we examined the alkyl transfer reactions of trialkylboranes to carbonyl compounds under electrochemical conditions.

The electrochemical reaction involving organoboranes was first reported by Suzuki et al.[5-7] As shown in Scheme 1, they showed that, in the divided electrolytic cell, propionitrile (1) was electrochemical reduced to the carbanion which coupled with R3B to provide various α-substituted propionitriles 2.

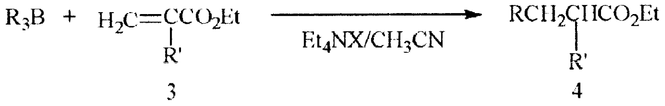


$$\underset{\mathbf{1}}{CH_3CH_2CN} + R_3B \xrightarrow[Et_4NI]{Pt\text{-}Pt/+e} \underset{\mathbf{2}}{CH_3\underset{R}{\underset{|}{C}}HCN}$$

R = n-butyl, hexyl, octyl, etc

Scheme 1

They also showed later on that R3B reacted with α,β-unsaturated esters **3** to give 1,4-addition products **4** upon electrolysis using divided cell in the presence of tetraalkylammonium halides as supporting electrolytes[8] (Scheme 2). The mechanism was suggested to involve generation of alkyl radical anions from trialkylboranes, and subsequent Michael type addition reactions.



$$R_3B + \underset{3}{H_2C{=}\underset{R'}{\underset{|}{C}}CO_2Et} \xrightarrow[Et_4NX/CH_3CN]{Pt\text{-}Pt/+e} \underset{4}{RCH_2\underset{R'}{\underset{|}{C}}HCO_2Et}$$

R = n-butyl, hexyl, octyl, etc X= Br, I, ClO$_4$
R'= H, CH$_3$

Scheme 2

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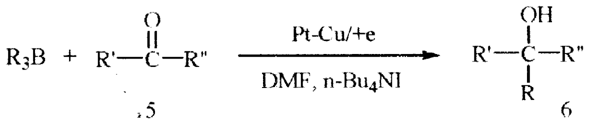
Based on the above results, we decided to investigate the electrochemical alkyl transfer reaction of trialkylborane with carbonyl compounds **5**. We conducted the electrochemical alkyl transfer reactions of trialkylboranes to carbonyl compounds at constant potential in undivided cell using sacrificial anode(copper) unlike the Suzuki's method at controlled current in divided cell. Scheme 3 outlines our electrochemical reaction systems where DMF(dimethylformamide) and Bu_4NI(tetrabutylammonium iodide) were used as a solvent and supporting electrolyte for the formation of the alcohols **6**.



R = ethyl, *sec*-butyl
R' = H, methyl, isopropyl, *sec*-butyl, phenyl
R" = methyl, pentyl, phenyl

Scheme 3

Our results are summarized in Table 1 and 2. The following procedure for preparation of 2-methyl-2-butanol represents our electrochemical reactions. The electrochemical reactions were carried out with EG & G PARC Model 173 and BAS 100β potentiostat. To a usual undivided cell equipped with platinum(2×2 Cm^2) as a working electrode and copper as a sacrificial anode, and magnetic stirrer unit were placed triethylborane(1 mmol, 1 mL of 1 M solution in THF), acetone(1 mmol, 0.17 mL), 20 mL of DMF and Bu_4NI(0.5 mmol, 0.18 g). The solution was electrolyzed at -3.2 V *vs.* SCE(saturated calomel electrode) of a cathode potential at room temperature under nitrogen atmosphere. The reaction mixture was frequently withdrawn by hypodermic syringe, quenched with 0.5 mL of saturated aqueous NH_4Cl solution. The mixture was diluted with 1 mL of diethyl ether, and saturated with NaCl. Upon addition of n-decane as an internal standard, the organic layer was analyzed with GC using a Chromosorb-WHP (10% Carbowax 20M) column, which indicated formation of 2-methyl-2-butanol in 68% yield after 9 h.

Under the above electrochemical conditions, only one of the three alkyl groups of trialkylborane was appeared to be transferred to carbonyl compounds. So, the yields of products were calculated based on the transfer of one alkyl group.

Table 1 showed transfer of ethyl group triethylborane to aliphatic ketones and aldehydes to give rise to the corresponding alcohols in 70-77% chemical yields. The alicyclic ketones were also converted into the corresponding alcohols in the yields of 73-77%. Comparable chemical yields(62-77%) were obtained with aromatic ketones and aldehydes. The sterically hindered tri-*sec*-butylborane required more negative reduction potential(-3.6 V) than triethylborane(-3.2 V). Under the conditions (Table 2), various alcohols were produced from the parent aldehydes and ketones in the range of 52-64% chemical yields.

Table 1. Alkyl Transfer Reaction with $Et_3B^{a,b}$

Trialkylborane	Substrate	Chemical yield[c](%)	Reaction time (h)
triethylborane	n-butyraldehyde	77	7
	trimethylacetaldehyde	70	6
	benzaldehyde	74	7
	4-chlorobenzaldehyde	70	9
	4-nitrobenzaldehyde	72	8
	p-anisaldehyde	73	8
	acetone	76	7
	3-methyl-2-butanone	75	7
	cyclohexanone	76	8
	cyclopentanone	77	8
	2-methylcyclohexanone	73	8
	4-*tert*-cyclohexanone	76	8
	4-methoxyacetophenone	77	8
	3-methoxyacetophenone	75	9
	4-chloroacetophenone	70	9
	3-chloroacetophenone	72	8
	benzophenone	64	9
	anthrone	62	10

[a] The electrochemical reactions were carried out at -3.2 V *vs.* SCE in undivided cell [b] The combination of 1 equiv of triethylborane and 1 equiv of substrate. [c] Chemical yields were estimated by GC.

Table 2. Alkyl Transfer Reaction with $(s\text{-}Bu)_3B^{a,b}$

Trialkylborane	Substrate	Chemical yield[c](%)	Reaction time (h)
tri-*sec*-butylborane	n-butyraldehyde	61	8
	trimethylacetaldehyde	63	8
	benzaldehyde	61	9
	p-anisaldehyde	60	10
	2-butanone	57	7
	acetophenone	56	9
	4-chloroacetophenone	59	9
	4-methoxyacetophenone	64	9
	benzophenone	52	10

[a] The electrochemical reactions were carried out at -3.6V *vs.* SCE in undivided cell. [b,c] See the corresponding footnote at Table 1.

No distinguishable differences in chemical yields were found between sterically different $(s\text{-}Bu)_3B$ and Et_3B, except that sterically more demanding $(s\text{-}Bu)_3B$ required higher electric potentials. However, the controlled cathodic potentials in dimethylformamide(DMF) and tetrabutylammonium iodide system adapted in these electrochemical reactions could be out of range or at most the upper end of limit, although these reactions cannot be clearly stated whether it proceeded via the similar type of radical process reported by Suzuki et al[5]. or not. However, we suspect that it would also proceed in through the formation of alkyl iodide from trialkylboranes by the reaction with iodine radicals generated at high voltage from tetrabutylammonium iodide, which then reacted further with the carbonyl compounds. Further study will be needed to understand the implication of the requirement of such high voltage for the reaction on the mechanism.

We are currently studying alkyl transfer reaction of tri-*tert*-alkylborane[9], triarylborane, and applying our methodology for stereoselective alkyl or aryl transfer reactions by using chiral alkylboranes such as diisopinocampheylborane species(Ipc_2B-R)[10], limonylborane species(LimB-R)[11].

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