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Communications

Electrochemical Alkyl Transfer Reactions of Trialkylboranes to Carbonyl Compounds by use of Aluminum Sacrificial Anode

Jung Hoon Choi[*], Jong Sung Youm, Cheon-Gyu Cho, Myung-Zoon Czae, Book Kee Hwang, and Jung Sung Kim[†]

[*]Department of Chemistry, Hanyang University, Seoul 133-791, Korea
[†]Department of Chemical education, Taegu University, Taegu 713-714, Korea

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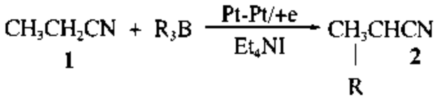
Many structurally diversed trialkylboranes, readily available from the parent alkenes *via* hydroborations,[1] have been effectively used for various synthetic transformations. For nucleophilic alkyl transfer reactions to carbonyl groups, however, only a few trialkylboranes were reported; they are tris(2-methylallyl)borane,[2] (3-trimethylsilyl)-allyl-dialkoxyboranes[3] and 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 by reduced to the carbanion which coupled with R3B to provide various substituted propionitriles **2**.

They also showed later on that R_3B 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.

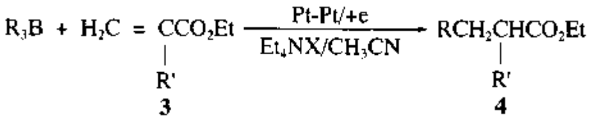


$$\underset{\mathbf{1}}{CH_3CH_2CN} + R_3B \xrightarrow[Et_4NI]{Pt\text{-}Pt/+e} \underset{R}{\underset{|}{CH_3CHCN}}\ \mathbf{2}$$

R=n-butyl, hexyl, octyl, etc

Scheme 1

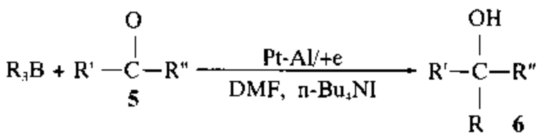
Based on the above results, we decided to investigate the electrochemical alkyl transfer reaction of trialkylborane with carbonyl compounds **5**. We conducted the electrochemical alkyl transfer reactions of trialkylboranes to carbonyl compounds at constant potential in undivided cell using sacrificial 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



$$R_3B + H_2C = \underset{\mathbf{3}}{\underset{R'}{\underset{|}{CCO_2Et}}} \xrightarrow[Et_4NX/CH_3CN]{Pt\text{-}Pt/+e} \underset{\mathbf{4}}{\underset{R'}{\underset{|}{RCH_2CHCO_2Et}}}$$

R=n-butyl, hexyl, octyl, etc X=Br, I, ClO_4
R=H, CH_3

Scheme 2



$$R_3B + R'-\underset{\mathbf{5}}{\overset{\overset{O}{|}}{C}}-R'' \xrightarrow[DMF,\ n\text{-}Bu_4NI]{Pt\text{-}Al/+e} R'-\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}-R''\ \mathbf{6}$$

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

Scheme 3

Table 1. Alkyl Transfer Reaction with Et$_3$B[a,b]

Trialkylborane	Substrate	Chemical yield[d] (%)	Reaction time (h)
triethylborane	trimethylacetaldehyde	55	14
	2-methylbutyraldehyde	60	15
	benzaldehyde	45	15
	4-chlorobenzaldehyde	52	13
	4-nitrobenzaldehyde	40	12
	cyclopentanone	45	11
	cyclohexanone	42	12
	2-methylcyclohexanone	40	10
	4-tert-cyclohexanone	47	10
	acetone	68	9
	acetophenone	47	12
	2-heptanone	65	8
	3-methyl-2-butanone	40	12
	isobutyroacetophenone	45	12
	4-methoxyacetophenone	45	15
	3-methoxyacetophenone	42	12
	4-chloroacetophenone	51	12
	3-chloroacetophenone	48	12
	benzophenone	39	15
	anthrone	35	12

[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. cChemical yields were estimated by GC.

the alcohols **6**.

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 aluminum 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$_4$NI (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$_4$Cl 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 55-70% chemical yields. The alicyclic ketones were also converted into the corresponding alcohols in the yields of 40-47%. Comparable chemical yields (35-52%) 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 30-52% chemical yields.

Table 2. Alkyl Transfer Reaction with (*sec*-Bu)$_3$B[a,b]

Trialkylborane	Substrate	Chemical yield[c] (%)	Reaction time (h)
tri-*sec*-butylborane	n-butyraldehyde	49	13
	trimethylacetaldehyde	42	15
	benzaldehyde	41	14
	p-anisaldehyde	37	12
	2-butanone	37	16
	acetophenone	32	13
	4-chloroacetophenone	46	12
	4-methoxyacetophenone	30	11
	benzophenone	52	10

[a] The electrochemical reactions were carried out at −3.6 V *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 (*sec*-Bu)$_3$B and Et$_3$B, except that sterically more demanding (*sec*-Bu)$_3$B 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 the reaction mechanism cannot be clearly stated whether it proceeded *via* the similar type of radical process reported by Suzuki *et al.*[5] or not, 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$_2$B-R),[10] limonylborane species (LimB-R).[11]

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Raman Spectroscopic Observation of the Intramolecular Interactions within the Poly(Ethylene Oxide) Unit in a Liquid Crystalline Molecule

Soo-Chang Yu*, Keunsik Ko, Keunok Han Yu, Jongwan Yu, Dong-Woo Lee†, and Myongsoo Lee†

Department of Chemistry, Kunsan National University, Kunsan, Chonbuk 573-701, Korea
†Department of Chemistry, Yonsei University, Sinchon 134, Seoul 120-749, Korea
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One of the most fascinating properties of rod-coil molecules consisting of a rigid rod and a flexible coil is their ability to microphase separate into a rich variety of ordered microstructures. Theoretical works have shown that the various supramolecular structures such as nematic, layed smectic, and cylindrical phases can be induced by temperature change depending on the relative volume fraction of blocks in rod-coil diblock systems.[1] With increasing the coil length, the microphase separation between each block occurs due to the large chemical differences between the stiff rod and flexible coil segments to form layered smectic assembly. As the coil length is further increased, molecular layers may collapse into discrete cylindrical micellar structures due to the modifications of the inter- or intramolecular interactions between the coil units.[2,3] The characteristic features of the inter- or intramolecular structure include structural regularity, bond flexibility, close packing ability, and interchain attraction.[4]

The overall chain shape related to the conformational distribution of the coil unit affects the inter- or intramolecular interactions depending on the nature of the coil unit. For example, the ordering of chain structure in cooperation with the secondary forces, such as hydrogen bonding, dipole interactions, or van der Waals interactions allows the chains to pack into a regular crystal lattice, and thus raises the crystalline melting point.[5] Therefore, the examination of the interactions in the coil units is necessary to have an insight into the physical properties of the rod-coil type liquid crystalline molecules.

This report will demonstrate for the first time that chain folding occurring within the long flexible coil unit of the liquid crystalline rod-coil molecule can induce phase transition via the change of intramolecular interaction. The investigation of the inter- or intramolecular interactions in the coil unit of a rod-coil liquid crystalline molecule was performed by using the Raman spectroscopic method, which is superior to other methods for the study of the motion of carbon backbones. Among the liquid crystalline molecules, a series of molecules with the following structure is selected;[6]

$CH_3O\text{-}(CH_2CH_2O)_n\text{-}C_6H_4C_6H_4COO\text{-}C_6H_4C_6H_4COO\text{-}(CH_2)_{21}\text{-}CH_3$

, where n=7, 12, 17, 22

Hereafter, the molecules of n=7, 12, 17, and 22 will be designated by 350-22, 550-22, 750-22, and 1000-22, respectively. These molecules are derivatives for the esterification product of ethyl 4-[4'-oxy-4-biphenylcarbonyloxy]-4'-biphenylcarboxylate with poly(ethylene oxide) (DP=12) (12-4), which is characterized previously by our group.[7,8] These molecules are of particular interest since they can form complexes with alkali metal cations through poly(ethylene oxide) chains to induce the various liquid crystalline supramolecular structures.

The corresponding Raman spectra are shown in Figure 1. The Raman bands in the range 800-900 cm^{-1} mostly assigned to the ethylene oxide modes except the 863 cm^{-1} band which is found to be originated from the methylene group.[7] For the PEO unit, although the sequence of the trans and gauch conformers is well characterized by the vibrational spectroscopy,[9] it is not easy to assign each band to a specific vibrational mode because of the variation of the Raman modes in different environments.

It is noteworthy that the 846 cm^{-1} band increases in intensity with increasing the coil length, while the other bands are not affected by the variation of coil length. The behavior of the 846 cm^{-1} band indicates that a large extent of conformational changes are related to the coil unit. Two possibile mechanisms can be accounted for the coil length-dependent variation of this band. One is due to the change in the intermolecular interactions between the neighboring

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*Author to whom correspondence should be addressed.