Electrochemical Organyl Group Transfer of Triorganylboranes to Carboxylic Acid Chlorides and Carboxylic Acid Anhydrides Using Copper Sacrificial Anode

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The organyl group transfer reaction of triorganylboranes with carboxylic acid chlorides or carboxylic acid anhydrides afford the corresponding ketones in moderate yields by electrochemical method using copper sacrificial anode in an undivided cell.

We recently demonstrated that the electrochemical organyl group transfer of triorganylboranes to carbonyl compounds by implementing an electrochemical procedure using copper as a sacrificial anode in an undivided cell.[1]

As soon as it published, this methodology had a great attention since of its enormous potentially synthetic utility.[2] The reaction can offer the wides scope for the further applications to various functional groups similar to Grignard reagent derived from alkyl halides.[3] Therefore, in an attempt to expand the scope in application, we examined the organyl group transfer reaction of organylboranes with carboxylic acid chlorides and carboxylic acid anhydrides to the corresponding ketones under electrochemical condition.

For the most purposes, the most convenient and versatile method for the triorganylborane involves the hydroboration of olefin with borane,[4] however triphenylborane could not be prepared by hydroboration and in this case Grignard reagents were utilized.[5]

First of all, a variety of degassed solvents, such as dimethylformamide (DMF) - tetrahydrofuran (THF) (2 : 1), acetonitrile (AN) - THF (2 : 1), and THF, anodes, such as copper, magnesium, zinc, aluminum, and electrolytes, such as tetrabutylammonium iodide (Bu$_4$NI), tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$) and lithium bromide (LiBr) with trihexylborane and benzoyl chloride was examined to find the combination which afford the best yield. As a result, it revealed that DMF - THF (2 : 1) as a solvent, Cu as a sacrificial anode and Bu$_4$NI as a electrolyte gave the best yield. Additionally, we found, although 4 cm^2 cathode area was adapted in our standard procedure because of reaction vessel capacity limit, that the reaction time significantly decreased with increasing their cathode surface area from 12 h at 4 cm^2 to 6 h at 9 cm^2 with similar yields, and electrochemical hexyl transfer reaction of trihexylborane was, especially, smoothly effected by addition of base, such as potassium *tert*-butoxide, resulting in decreasing of reaction potential from −3.2 V to −2.6 V.

And all the following reactions illustrated in Table 2 undertook under our standard condition (platinum (2×2 cm^2), copper (2×2 cm^2), DMF - THF (2 : 1), Bu$_4$NI, KOC (CH$_3$)$_3$), which was optimized in above experiments
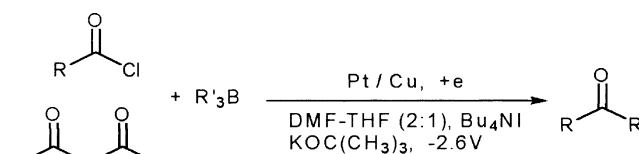
Scheme 1

Table 1. Optimization of electrochemical hexyl transfer reaction condition of trihexylborane to benzoyl chloride[a,b,c]

Sacrificial anode	Solvent	Electrolyte	Base	Ketone (%)[d]	Reaction time (h)[d]	Alcohol (%)[d]	Coupling (%)[d]
Cu	DMF-THF (2:1)	Bu$_4$NI	KOC(CH$_3$)$_3$	73	12	5	6
Zn	DMF-THF (2:1)	Bu$_4$NI	KOC(CH$_3$)$_3$	64	24	3	2
Al	DMF-THF (2:1)	Bu$_4$NI	KOC(CH$_3$)$_3$	64	36	6	9
Mg	DMF-THF (2:1)	Bu$_4$NI	KOC(CH$_3$)$_3$	58	60	5	12
Cu	THF	Bu$_4$NI	KOC(CH$_3$)$_3$	47	36	3	8
Cu	AN-THF (2:1)	Bu$_4$NI	KOC(CH$_3$)$_3$	trace	30	trace	13
Cu	DMF-THF (2:1)	Bu$_4$NBF$_4$	KOC(CH$_3$)$_3$	41	36	4	15
Cu	DMF-THF (2:1)	LiBr	KOC(CH$_3$)$_3$	trace	60	trace	24
Cu	DMF-THF (2:1)	Bu$_4$NI	NaOC$_2$H$_5$	69	18	6	3
Cu	DMF-THF (2:1)	Bu$_4$NI	BHT-Na[g]	64	15	4	5
Cu[e]	DMF-THF (2:1)	Bu$_4$NI	KOC(CH$_3$)$_3$	70	20	6	5
Cu[f]	DMF-THF (2:1)	Bu$_4$NI	KOC(CH$_3$)$_3$	68	6	8	4

[a]The electrochemical reactions were carried out at −2.6 V *vs.* Ag/AgCl in an undivided cell at room temperature. [b]Combination of 1 equiv of trihexylborane and 1 equiv of benzoyl chloride. [c]Solvent (12 mL), trihexylborane (2 mmol), benzoyl chloride (2 mmol), electrolyte (0.5 mmol), base (2 mmol), Pt cathode (2×2 cm^2) and sacrificial anode (2×2 cm^2). [d]Chemical yields were estimated by GC. [e]Surface area of Pt cathode is 1 cm^2. [f]Surface area of Pt cathode is 9 cm^2. [g]Sodium 2,6-Di-*tert*-butyl-4-methylphenoxide

(Scheme 1).

In all the cases of electrochemical organyl group transfer reactions under our standard condition, products (the corresponding alcohols) formed by two equiv of organyl group transfer to substrate together with products (the corresponding hydrocarbons) produced by coupling of organyl groups of triorganylboranes as minor products were formed as well as products (the corresponding ketones) generated by one organyl group transfer to substrate as major products.

When electrochemical primary alkyl transfer reaction of trialkylborane, trihexylborane, was conducted with aliphatic carboxylic acid chlorides, propionyl chloride, and aromatic carboxylic acid chloride, benzoyl chloride, the desired ketones were obtained in the range of 71-73% yields in 12 h.

For electrochemical *sec*-alkyl transfer of trialkylborane, tri-*sec*-butylborane, to carboxylic acid chlorides, similar to those for primary trialkylborane except the subtle decrease of yields of desired ketones, all the carboxylic acid chlorides and carboxylic acid anhydrides adapted in our experiments were converted into the corresponding ketones in the range 67-69% yields in 12 h.

In the occasion of electrochemical aryl transfer of triarylborane, triphenylborane, to carboxylic acid chlorides and carboxylic acid anhydrides, there were no significant differences from those for trialkylboranes both in yields and reaction rates.

In view of the results so far achieved, the experiments showed that no distinguishable differences in chemical yields and reaction rate according to any structural changes both of triorganylboranes and substrates. And, although the absence of any systematic study to find out the mechanism, the most likely mechanism of organyl transfer reaction involves the nucleophilic addition of electrochemically generated organyl anions, which would be formed possibly through radical stage that could be deduced by resulting in the formation of coupling products.

In conclusion, it might be possible that this electrochemical reaction can provide a good synthetic methodology for anyone interested in making use of the enormous synthetic potential of organoboranes. However, it must be noticed that there is room for further improvement of the chemical yield by introducing some catalysis into electrochemical reaction mixture.

The following procedure for preparation of heptanophenone represents our electrochemical reactions. The electrochemical reactions were carried out with EG & G PARC Model 173, BAS 100b and Electrolysis Model C-600 cell potentiostat. To an 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 benzoyl chloride (0.281 g, 2 mmol), 8 mL of DMF and Bu$_4$NI (0.185 g, 0.5 mmol). The mixture of potassium *tert*-butoxide (0.224 g, 2 mmol) and trihexylborane (2 mL of 1 M solution in THF, 2 mmol) and additional 2 mL of THF were introduced by hypodermic syringe dropwise for 1 h. Then the solution was electrolyzed at -2.6 V *vs*. Ag/AgCl reference electrode of cathode potential at room temperature under nitrogen atmosphere. The reaction mixture was withdrawn by hypodermic syringe at appropriate interval, quenched with 2 mL of saturated NH$_4$Cl solution. The mixture was diluted with 5 mL of diethyl ether and saturated with NaCl. Upon addition of n-tetradecane as an internal standard, the organic layer was analyzed with GC using a Chromosorb-WHP (10% SE-30) column, which indicated to formation of heptanophenone in 73% yield in 12 h.

Table 2. The electrochemical organyl transfer of triorganylboranes to carboxylic acid chlorides and carboxylic acid anhydrides[a,b,c]

Triorganylborane	Substrate	Ketone (%)[d]	Reaction time (h)	Alcohol (%)[d]	Coupling (%)[d]
Trihexylborane	Propionyl chloride	71	12	8	4
	Benzoyl chloride	73	12	5	6
	Propionic anhydride	65	12	4	9
	Benzoic anhydride	62	12	2	14
Tri-secbutylborane	Propionyl chloride	69	12	8	5
	Benzyoyl chloride	67	12	5	6
	Propionic anhydride	61	12	6	10
	Benzoic anhydride	62	12	2	11
Triphenylborane	Propionyl chloride	70	12	3	5
	Benzoyl chloride	71	12	1	7
	Propionic anhydride	61	12	2	8
	Benzoic anhydride	63	12	trace	12

[a]The electrochemical reactions were carried out at -2.6V *vs*. Ag/AgCl in an undivided cell at room temperature. [b]Combination of 1 equiv of triorganylborane and 1 equiv of substrate. [c]DMF (8 mL) - THF (4 mL), R$_3$B (2 mmol), substrate (2 mmol), Bu$_4$NI (0.5 mmol), KOC(CH$_3$)$_3$ (2 mmol), Pt cathode (2×2 cm^2) and Cu anode (2×2 cm^2). [d]Chemical yields were estimated by GC.

References

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