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Formation of a Novel Acyl Anion Equivalent by the Electroreduction of Oxazolinium Salts[1)]

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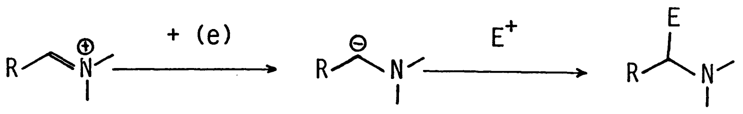
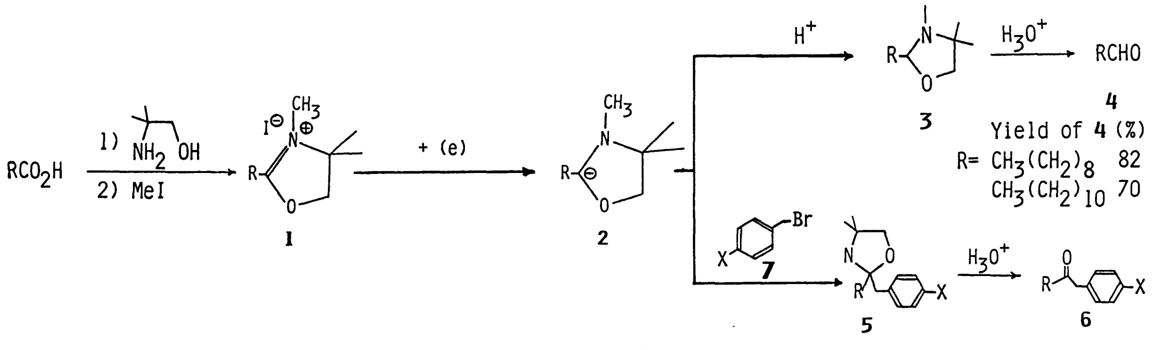
Electroreduction of oxazolinium salts synthesized from the corresponding carboxylic acids gave a novel acyl anion equivalent (AAE). The reaction of these AAEs with electrophiles afforded the corresponding aldehydes or ketones in good yields.

The electrochemical method is one of the most reliable tools for inversion of polarity of organic compounds since in the two electrons reduction of an electrophile (E^+), for instance, the polarity of E^+ is inverted to a nucleophile (Nu^-) by donation of two electrons to E^+. Our previously reported electroreduction[2-5)] of iminium salts (E^+) to Nu^- is typical such an example.



When the iminium salt is suitably designed, a novel acyl anion equivalent (AAE) seems to be generated. Here, we wish to report that the electroreduction of oxazolinium salts led to the formation of such AAEs and the reaction of these AAEs with electrophiles would be useful for the transformation of carboxylic acids to the corresponding aldehydes and ketones.

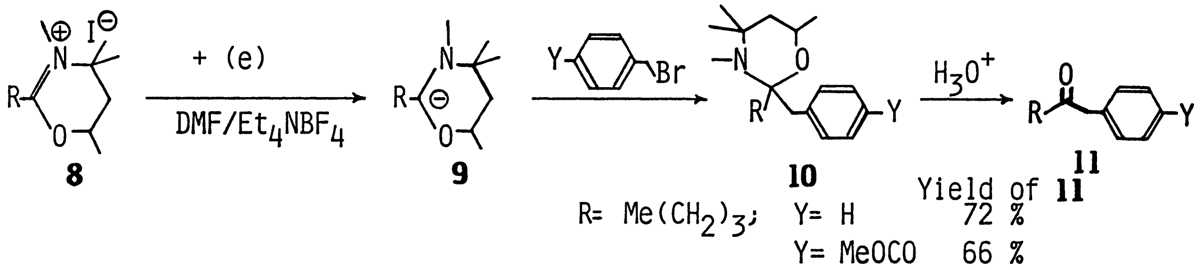
As shown in Scheme 1, oxazolinium salts 1 were synthesized from the corresponding carboxylic acids by a known method.[6,7)] The electroreduction[8)] of a DMF solution of 1 in the presence of methanesulfonic acid as a proton source resulted in the formation of an N,O-acetal 3 of the corresponding aldehyde 4. These results suggest the intermediary formation of AAE 2. Thus, the electroreduction of 1 in



Scheme 1.

the presence of benzyl halides 7 gave N,O-acetals 5 of the corresponding ketones 6 through the reaction of the intermediate 2 with 7.

Typical procedure is as follows: Into a cathodic chamber of a cell equipped with a lead cathode[9] (4 cm^2) was put a solution of 1 (5 mmol), electrophile ($MeSO_3H$ or benzyl halide) (10 mmol), and Et_4NOTs (5 mmol) in DMF (20 ml). The anodic solution was 15 ml of DMF containing 6 mmol of Et_4NOTs, and a platinum plate (4 cm^2) was used as an anode. After 4 *F*/mol of electricity was passed under constant current conditions (0.2 A), the product 3 was separated by usual working-up. Hydrolysis[10] of 3 gave 4 in good yields. As shown in Table 1, this reaction is applicable to the synthesis of benzylic ketones having a variety of functional groups such as ester (runs 2 and 6), halide (run 5), and nitrile (run 4). Similar AAEs 9 are also formed by the cathodic reduction of oxazinium salts 8, and they are alkylated by the reaction with benzyl halides (Scheme 2).



Scheme 2.

Table 1. Electroreduction of Oxazolinium Salt

Run	1 R =	7 X =	5 Yield/%[a,b]	Run	1 R =	7 X =	5 Yield/%[a,b]
1	$PhCH_2CH_2$	H	83	4	$Me(CH_2)_2$	CN	61
2	$PhCH_2CH_2$	CO_2Me	76	5	$Me(CH_2)_2$	Cl	70
3	$Me(CH_2)_2$	H	81	6	$MeOCO(CH_2)_7$	H	71

a) Isolated. b) The structures of the products were determined by spectroscopic and elemental analyses.

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8) Reduction potentials fo 1 were E_p = -1.50 — -1.60 V *vs.* SCE.
9) Electroreductive transformation of 1 to 5 was carried out using an aluminum cathode, and a lead plate was put into the cathodic chamber.[2]
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