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MICHAEL ADDITION OF NOVEL ACYL ANION EQUIVALENTS GENERATED BY THE ELECTROREDUCTION OF OXAZOLINIUM SALTS TO ACTIVATED OLEFINS[1]

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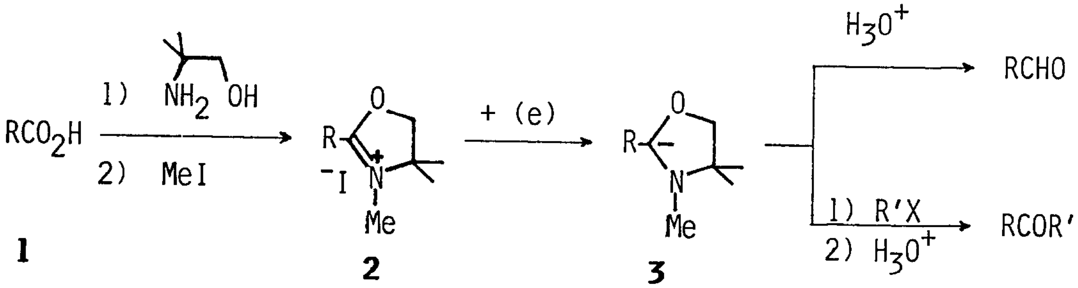
Summary: Electroreduction of oxazolinium salts gave novel acyl anion equivalents (AAEs), and the Michael addition of these AAEs to activated olefins has been found to be promoted effectively by the addition of chlorotrimethylsilane into the reaction system. This reaction was applied to the synthesis of *cis*-jasmone and dihydrojasmone.

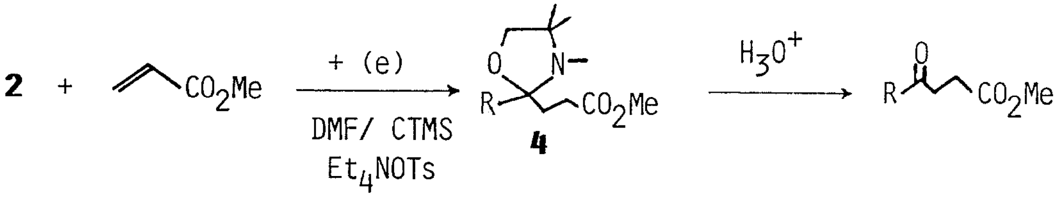
Although acyl anion equivalents (AAEs) are useful intermediates in organic synthesis,[2] the design and synthesis of precursors of the AAE are not always easy and the formation of AAE from the precursors often requires strong bases. We have recently found[3] that novel AAEs 3 are formed by electroreduction of oxazolinium salts 2 which are easily synthesized from the corresponding carboxylic acids 1, and ketones or aldehydes are easily prepared from 3.



In this report, we wish to describe our new finding that the electroreduction of 2 in the presence of chlorotrimethylsilane (CTMS) and activated olefins gave the addition products of 3 to the activated olefins.

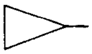
As shown in Scheme 1, electroreduction of a solution of an oxazolinium salt[4] 2 and methyl acrylate in DMF using Et_4NOTs as a supporting electrolyte did not give the addition product 4, while the addition of CTMS[5] to the reaction system resulted in the formation of 4 in a good yield. This reaction was applied to the synthesis of a variety of γ-keto esters and other related compounds as the results are summarized in Table 1.

Electroreduction of a DMF solution of 2 and methyl vinyl ketone under the same reaction conditions, however, brought about a low yield of the addition product 5, whereas the use of Bu_4NBF_4 instead of Et_4NOTs as a supporting electrolyte yielded 5 in a reasonable yield (Scheme 2).



Scheme 1

Table 1. Synthesis of N,O-Acetal of γ-Keto Ester and γ-Keto Nitrile

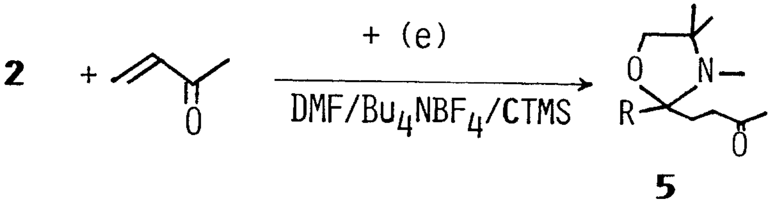
	Oxazolinium Salt 2	Activated Olefin			
Run	R =	R^1=	R^2=	X=	Product Yield (%)[a,b]
1	$PhCH_2CH_2$	H	H	CO_2Me	68
2	"	H	H	"	trace[c]
3	"	H	Me	"	65
4	"	Me	H	"	61
5	"	Me	H	"	50[d]
6	$Me(CH_2)_2$	H	Me	"	74
7	$Me(CH_2)_5$	H	H	"	76
8	$Me(CH_2)_8$	Me	H	"	68
9	$Me(CH_2)_{10}$	H	H	"	73
10		H	H	"	77
11	$PhCH_2CH_2$	CO_2Me	H	"	40
12	"	H	CH_2CO_2Me	"	58
13	"	H	H	CN	44

a) Isolated yields of corresponding N,O-Acetals.

b) All the products gave satisfactory spectroscopic values and elemental analyses.

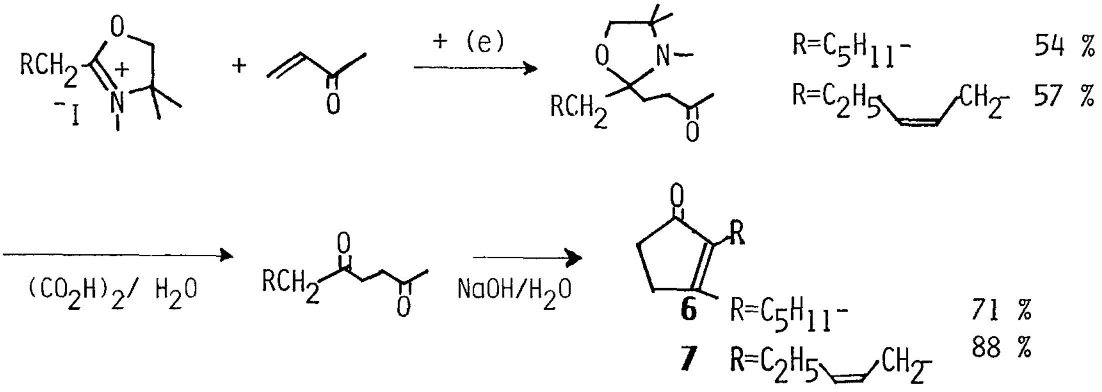
c) Cathodic reduction was carried out in the absence of CTMS.

d) Bu_4NBF_4 was used as a supporting electrolyte.



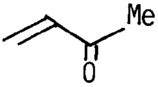
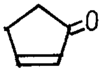
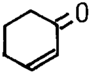
Scheme 2

As shown in Table 2, this method is applicable to the preparation of a variety of N,O-acetals of 1,4-diketones, and hence, the synthesis of dihydrojasmone (6) and *cis*-jasmone (7) is easily accomplished (Scheme 3) by utilizing this reaction.



Scheme 3

Table 2. Electroreductive Formation of N,O-Acetal of 1,4-Diketone

Run	Oxazolinium Salt 2 R =	Ketone	Product Yield (%)[a,b]
1	$PhCH_2CH_2$		13[c]
2	"	"	40[d]
3	"		52[d]
4	"		58[d]

a) Isolated yields.

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

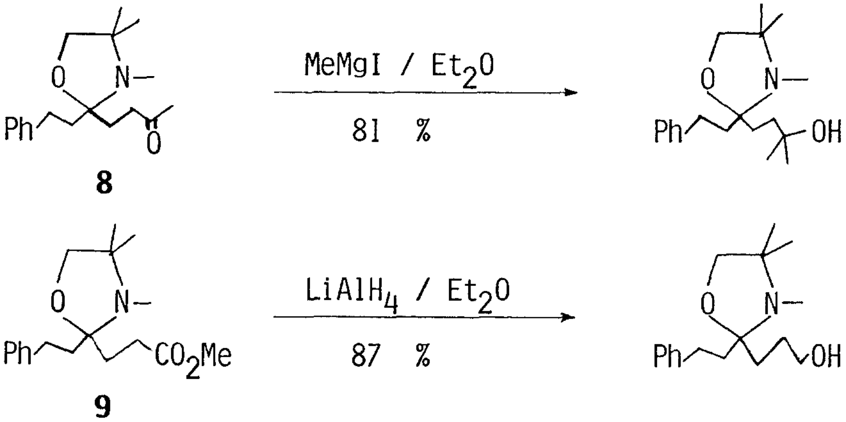
c) Et_4NOTs was used as a supporting electrolyte.

d) Bu_4NBF_4 was used as a supporting electrolyte.

A typical procedure for the addition of 3 to the activated olefins is as follows: A solution of an oxazolinium salt (5 mmol), Et_4NOTs (5 mmol), and an activated olefin (20 mmol) in dry DMF was used as catholyte. Anolyte was a solution of Et_4NOTs (6 mmol) in dry DMF. The electroreduction was carried out at room temperature using a lead cathode (4 cm^2) and a platinum anode (4 cm^2), and a DMF solution of CTMS (20 mmol) was added dropwise into the cathodic chamber over the period of the electroreduction. In the synthesis of 5, Bu_4NBF_4

was used as the supporting electrolyte. A constant current electricity (0.2 A) was passed until almost all of the starting material 2 were consumed (ca. 3 F/mol), and then the product were isolated by the usual method.

Since one of the carbonyl groups of the product 1,4-diketone 8 or γ-keto ester 9 is selectively protected as N,O-acetal in this reaction, further transformation such as LAH reduction and the Grignard reaction of another carbonyl group are easily attained (Scheme 4) without any change at the protected carbonyl group.



Scheme 4

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References and Notes

1. Electroorganic Chemistry. 110.
2. D. Seebach, *Angew. Chem.*, 91, 259 (1979).
3. T. Shono, S. Kashimura, Y. Yamaguchi, and F. Kuwata, the Annual Meeting of the Electrochemical Society of Japan, Yokohama, October 1985, Abstr. E313, p. 301.
4. Reduction potentials of 2 were $E_p = -1.5 \sim -1.6$ V *vs.* SCE.
5. We have previously reported that the cathodic coupling reaction[6] of activated olefins with ketones or aldehydes is promoted by the addition of CTMS into the reaction system.
6. T. Shono, H. Ohmizu, S. Kawakami, and H. Sugiyama, *Tetrahedron Lett.*, 21, 5029 (1980).

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