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Selective Coupling of Non-Activated Olefins with Ethyl Cyanoacetate by Mn^{3+}-Mediated Anodic Oxidation

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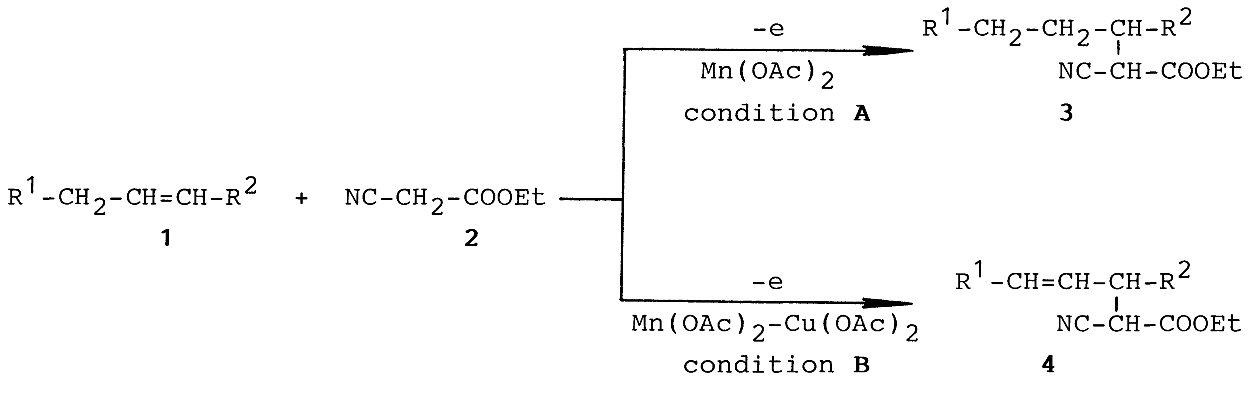
Novel carbon-carbon bond formation of non-activated olefins with ethyl cyanoacetate has been developed by anodic oxidation using only a small amount of $Mn(OAc)_2 \cdot 4H_2O$ to give selectively either saturated or unsaturated coupling products depending upon the presence of a catalytic amount of $Cu(OAc)_2 \cdot H_2O$.

Manganese triacetate($Mn(OAc)_3 \cdot 2H_2O$) has been often used as a conventional reagent for oxidative carbon-carbon bond formation such as formation of dihydrofuranes,[1a)] carbolactonization of olefins,[2)] and coupling of olefins with aldehydes or ketones.[3-5)] The synthetic utility of this method, however, has been considerably limited because of less reproducibility of the results, possibly due to much sensitivity of $Mn(OAc)_3 \cdot 2H_2O$ toward water and oxygen,[2a,6)] employment of at least 2 equiv. moles of this relatively unstable metal-salt having rather high molecular weight relative to those of olefins and products, and troublesome treatment of the resulting



large amount of $Mn(OAc)_2 \cdot 4H_2O$.

In this communication, we wish to present Mn^{3+}-mediated coupling of non-activated olefins (**1**) with ethyl cyanoacetate (**2**) by indirect electrooxidation in the presence of only a small amount of stable and easily available $Mn(OAc)_2 \cdot 4H_2O$, which may be electrochemically oxidized to a Mn^{3+}-species, an active oxidizing reagent in the reaction system,7) to give the corresponding α-saturated alkyl cyanoacetates **3** (condition **A**). It is quite noteworthy that addition of a catalytic amount of $Cu(OAc)_2 . H_2O$ brought about dramatic change in the formation of the products to give the corresponding α-allylic adducts **4** selectively (condition **B**).

A typical procedure is as follows : A solution of 4.92 g (60 mmol) of anhydrous sodium acetate in 80 ml of the mixed solvent of glacial acetic acid and ethyl acetate (volume ratio 13:3) was placed in anodic and cathodic chambers of a divided cell equipped with carbon rod electrodes as an anode and a cathode, and a ceramic cylinder as a diaphragm. To the anolyte were added 0.49 g (2 mmol) of $Mn(OAc)_2 \cdot 4H_2O$, 0.82 g (10 mmol) of cyclohexene (**1e**) and 3.39 g (30 mmol) of **2** (Under the condition **B**, 0.10 g (1 mmol) of $Cu(OAc)_2 . H_2O$ was also added.). The electrolysis was carried out under the constant-current conditions (current density : 2.0-3.0 A/dm^2) at 40 °C with magnetic stirring until 2 F/mol of electricity based on **1e** was passed through the system. The usual work-up followed by column chromatography of the crude product mixture over silica gel (elute : $n-C_6H_{14}/EtOAc = 9/1$) afforded ethyl cyclohexylcyanoacetate (**3e**) as a single product in a 60% yield (1.17 g) based on **1e** (Under the condition **B**, ethyl (2-cyclohexyl)

Table 1. Mn^{3+}-Mediated Anodic Coupling of Non-Activated Olefins **1a-h** with Ethyl Cyanoacetate **2**

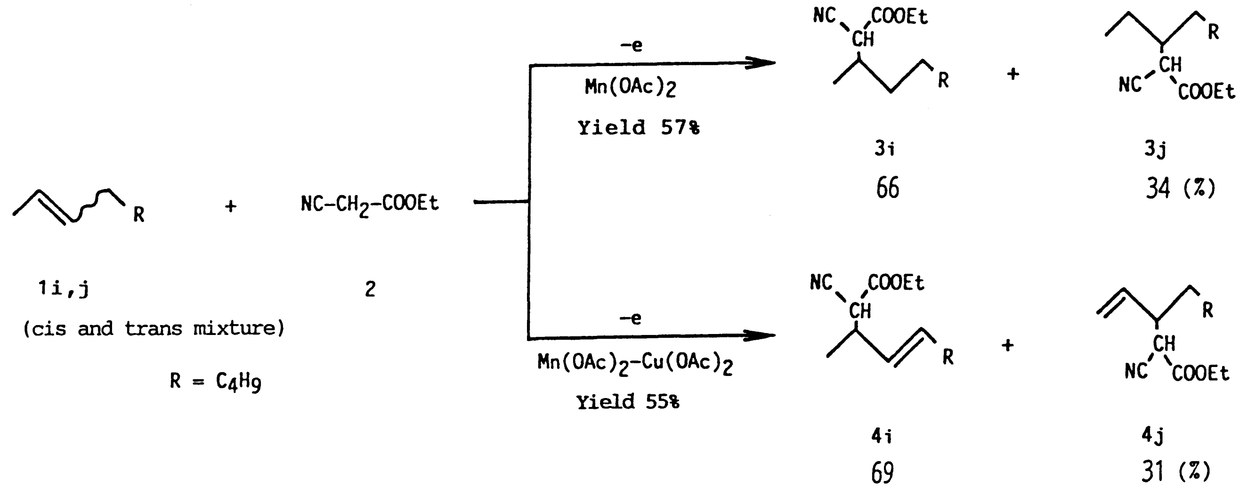
Olefin **1** R^1	R^2		Yield of products/%a),b) condition **A**	condition **B**
$CH_3-(CH_2)_2-$	H	(**1a**)	62 (**3a**)	45 (**4a**)c)
$CH_3-(CH_2)_4-$	H	(**1b**)	54 (**3b**)	55 (**4b**)c)
$CH_3-(CH_2)_6-$	H	(**1c**)	56 (**3c**)	58 (**4c**)c)
$-(CH_2)_2-$		(**1d**)	64 (**3d**)	44 (**4d**)
$-(CH_2)_3-$		(**1e**)	60 (**3e**)	53 (**4e**)
$-(CH_2)_4-$		(**1f**)	51 (**3f**)	54 (**4f**)
$-(CH_2)_5-$		(**1g**)	60 (**3g**)	47 (**4g**)
$-(CH_2)_9-$		(**1h**)	50 (**3h**)	49 (**4h**)

a) Satisfactory spectroscopic analytical results (IR, ^1H-NMR, and MS) were obtained for all the products **3a-h** and **4a-h**. b) Isolated yields based on the olefins **1**, which have not been optimized as yet. c) The products **4a-c** were found to consist of a (E)-stereoisomer exclusively.

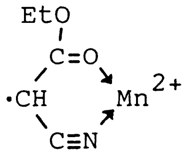
cyanoacetate (**4e**) was obtained as a main product in a 53% yield accompanying only a trace amount of **3e.**).[8]

Under the similar conditions, Mn^{3+}-mediated indirect anodic oxidation brought about the carbon-carbon bond formation between a variety of non-activated olefins **1** and ethyl cyanoacetate(**2**) to give selectively either the corresponding saturated or unsaturated coupling products, **3a-h** or **4a-h**, in good to moderate yields depending upon the presence of a catalytic amount of $Cu(OAc)_2 \cdot H_2O$.

It is interesting that the present oxidative carbon-carbon bond formation took place regioselectively according to the Markownikoff's rule as shown for the reaction of **1a-c.** On the other hand, treatment of 2-octene (cis (**1i**) and trans (**1j**) mixture) as an olefin under the similar condition **A** led to the formation of a mixture consisting of 2-octyl and 3-octyl adducts (**3i,j**) in the ratio of 66:34. The similar phenomenon was observed for the reaction under the condition **B** to give a mixture of 2-(3-octenyl) and 3-(1-octenyl)adducts (**4i,j**) in the ratio of 69:31. These results may indicate that regioselectivity of the carbon-carbon bond formation in the present electrooxidation is principally attributed to steric effect as well as stability of the generating intermediates. It may be also noteworthy that only (E)-allylic coupling products, **4a-c** and **4i** were obtained from the reaction of **1a-c** and **1i,j** with **2** under the condition **B.**



Although a detailed mechanism of the present Mn^{3+}-mediated coupling has not been clear as yet, the remarkable steric effect[8] may suggest the generation of a Mn^{2+}-complexed methine radical species (**5**) from the reaction[5,9] of the electrogenerated Mn^{3+}-ion[10] with **2.** Presence of $Cu(OAc)_2 \cdot H_2O$ may remarkably accelerate further oxidation of the radical intermediates (**6**) to the corresponding organocopper complexes[11] followed by β-elimination to give the unsaturated coupling products **4**. Further study on the present Mn^{3+}-mediated anodic coupling is in progress.



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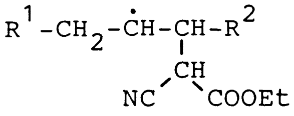

$R^1\text{-}CH_2\text{-}\dot{C}H\text{-}CH(CH(CN)COOEt)\text{-}R^2$

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