Tetrahedron Vol. 47, No. 4/5, pp. 831-840, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

CARBON-CARBON BOND FORMATION USING MANGANESE(III) ACETATE AS AN ELECTROCHEMICAL MEDIATOR

Ryushi Shundo+, Ikuzo Nishiguchi*,[1], Yoshiharu Matsubara+,
and Tsuneaki Hirashima

Osaka Municipal Technical Research Institute,
1-6-50, Morinomiya, Jyoto-ku, Osaka 536, JAPAN
+Department of Applied Chemistry, Faculty of Science and Engineering
Kinki University, 3-4-1, Kowakae, Higashi-Osaka 577, JAPAN

(*Received in USA* 24 *August* 1990)

Abstract:

Anodic oxidation in a solution containing a variety of olefins and a small amount of $Mn(OAc)_2{\cdot}4H_2O$ brought about Mn^{+3}-mediated carbon-carbon bond formation, such as efficient carboxymethylation of styrene derivatives to the corresponding γ-aryl-γ-butyrolactones, and selective coupling of active methylene compounds with non-activated monoolefins, unconjugated dienes or 5-arylpent-1-enes.

Introduction

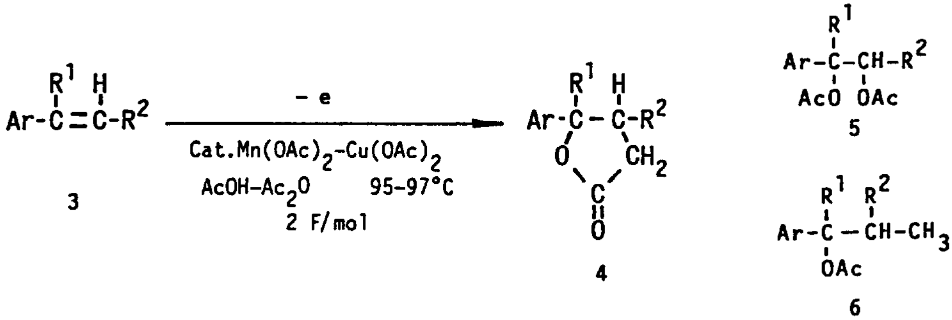
In spite of high potentiality[2)] of $Mn(OAc)_3{\cdot}2H_2O$(**1**) for oxidative carbon-carbon bond formation, practical usefulness of Mn^{+3}-promoted oxidation in organic synthesis has been considerably limited because of instability[3)] of the manganese (III) salt **1** , employment of at least 2 equivalent moles (based on substrates) of the salt **1** having a rather high molecular weight relative to those of substrates or products, and troublesome treatment of the resulting large amount of $Mn(OAc)_2{\cdot}4H_2O$(**2**).

In this study, we wish to demonstrate that anodic oxidation in a solution containing a variety of olefins and a small amount of $Mn(OAc)_2{\cdot}4H_2O$(**2**) brought about selective and efficient Mn^{+3}-mediated carbon-carbon bond formation, which may be characterized by no need for use of the unstable Mn^{+3}-salt **1** and for treatment of the resulting stable Mn^{+2}-salt **2** , better yield, employment of only small amounts of easily available Mn^{+2}-salt (**2**) (1/10-1/3 equivalent moles based on a substrate), electrochemically oxidized to the active Mn^{+3} species <u>in situ</u>.

Results and Discussion

1. Carboxymethylation of Styrene Derivatives to γ-Aryl-γ-lactones

Mn^{3+}-mediated electrooxidation in a mixed solvent of glacial acetic acid and acetic anhydride containing styrene derivatives(**3**) and a small amount of **2** was found to result in efficient carboxymethylation to give the corresponding γ-aryl-γ-lactones (**4**) as the main products in good yields, accompanying small amounts of 1-aryl-2,3-diacetoxyethane(**5**) and 1-acetoxyarylpropanes(**6**) as by-products.



The electrolysis was generally carried out at 95-97°C with magnetic stirring under constant current conditions in a beaker-type of divided cell equipped with carbon rods as anode and cathode, and a ceramic cylinder as a diaphragm. The yields of the products **4**, **5** and **6** were

Table 1. Carboxymethylation of Styrene Derivatives by Mn^{+3}-Mediated Electrooxidation[a)]

Styrene Derivative				C.E.(%)[b)] of the products		
Ar	R^1	R^2		4	5	6
C_6H_5	H	H	(3a)	80 (75)[c)]	8	-[d)]
C_6H_5	CH_3	H	(3b)	75 (74)[c)]	-[d)]	-[d)]
C_6H_5	H	C_6H_5	(3c)	61 (16)[c)]	3	-[d)]
p-ClC_6H_4	H	H	(3d)	58	16	5
p-$CH_3C_6H_4$	H	H	(3e)	81	7	-[d)]
C_6H_5	H	COOEt	(3f)	84 (45)[c)]	-[d)]	-[d)]
C_6H_5	H	CH_2OH	(3g)	78	-[d)]	-[d)]
C_6H_5	H	$-CH_2-$	(3h)	63	23	-[d)]

a) The electrolysis was carried out in a mixed solvent of AcOH(50ml) and Ac_2O(25ml) containing an olefin(90mmol), $Mn(OAc)_2 \cdot 4H_2O$(5.8mmol), $Cu(OAc)_2 \cdot H_2O$(2.2mmol), and AcONa(61mmol). b) Current yield. Current yield was obtained when 36mF of electricity(a theoretical amount(2.0 F/mol) for 18 mmol of a starting olefin) was passed. c) Reported yield of the conventional method[5)] based on the Mn^{3+} salt 1 d) Non-detected.

considerably dependent upon current density, nature and amount of additives and supporting electrolytes. It was found that relatively low current density, use of sodium acetate as a supporting electrolyte, and presence of a catalytic amount of cupric acetate in addition of manganese (II) diacetate were requisite for effective formation of the desired product **4** in this anodic reaction.

Efficient carboxymethylation was similarly found for a variety of styrene derivatives **3a-g** under the standard conditions, as shown in Table 1.[4] The numbers in the **parentheses** of Table 1 show the reported yields of the product **4** based on $Mn(OAc)_3 \cdot 2H_2O$(**1**) used, indicating some superiority of the present electrochemical oxidation to the conventional methods[5] using a stoichiometric amount of the Mn^{+3}-salt **1**, especially in the reaction of stilbene **3c** and ethyl cinnamate **3f**.

2. Selective Carbon-Carbon Bond Formation between Non-Activated Olefins and Active Methylene Compounds by Mn^{+3}-Mediated Electrooxidation[6]

Recently some examples[7] have been reported for the coupling of non-activated olefins(**7**) with active methylene compounds in contrast with much usefulness of the base-catalyzed addition of those compounds to activated olefins.[8]

In this study, Mn^{+3}-mediated oxidative coupling of various non-activated olefins(**7**) with active methylene compounds such as acetoacetate(**8**), ethyl cyanoacetate(**9**), and diethyl malonate(**10**) has been developed by indirect anodic oxidation using a small amount of stable and easily available $Mn(OAc)_2 \cdot 4H_2O$(**2**). For example, ethyl 2-alkyl cyanoacetates(**11**) were obtained as the sole products from electrooxidation of the mixture of simple olefins(**7**) and **9** in the mixed solvent of acetic acid and ethyl acetate containing 0.2 equivalent mole of the Mn^{+2}-salt **2** and sodium acetate as a supporting electrolyte at 40°C using a divided electrolysis cell equipped with a ceramic cylinder as a diaphragm and carbon rods as anode and cathode, until 2.0 F/mol of electricity passed through the system(condition **A**). It may be noteworthy that the addition of a catalytic amount of $Cu(OAc)_2 \cdot H_2O$ under the same reaction conditions brought about dramatic change in the formation of the product to give the corresponding ethyl α-allylic cyanoacetate(**12**) selectively(condition **B**).

Table 2 shows the results on highly selective formation of either the saturated or unsaturated coupling products, **11** or **12**, depending upon the presence of $Cu(OAc)_2 \cdot H_2O$, between a variety of non-activated olefins(**7**) and ethyl cyanoacetate(**9**) by the present Mn^{3+}-mediated indirect anodic oxidation.

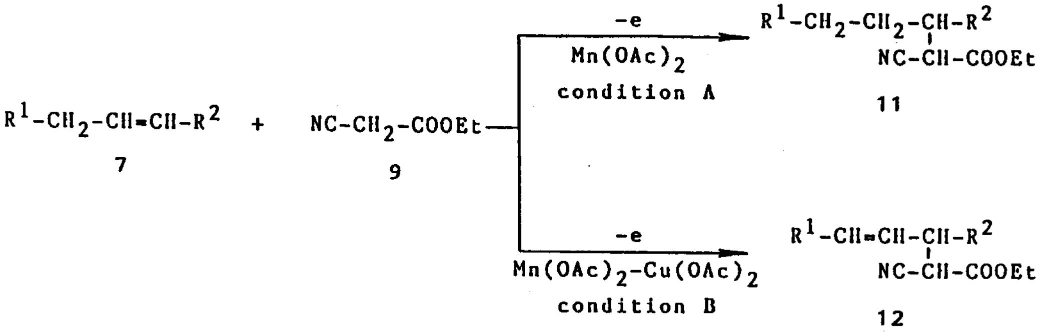
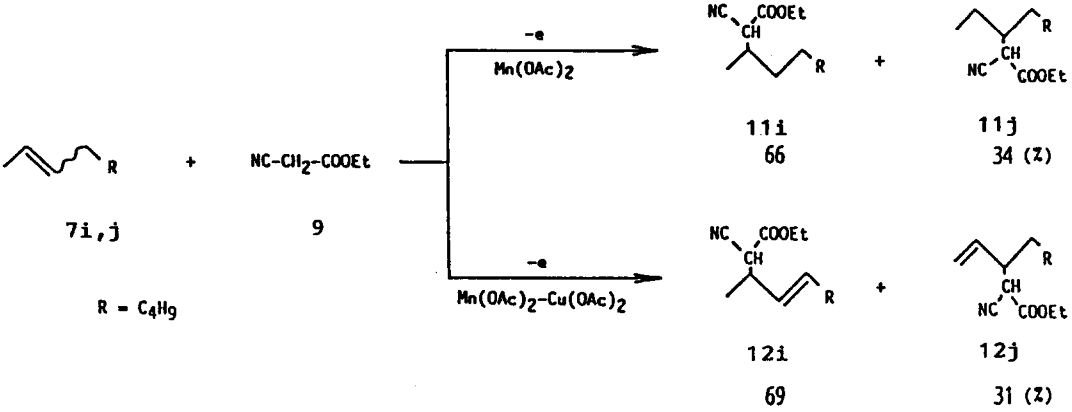


Table 2. Mn^{+3}-Mediated Anodic Coupling of Non-activated Olefins **11a-h** with Ethyl Cyanoacetate **9**

Olefin			Yield (%) of Products[a),b)]			
R^1	R^2		Condition A		Condition B	
$CH_3(CH_2)_2-$	H	(**7a**)	62	(**11a**)	45	(**12a**)[c)]
$CH_3(CH_2)_4-$	H	(**7b**)	54	(**11b**)	55	(**12b**)[c)]
$CH_3(CH_2)_6-$	H	(**7c**)	56	(**11c**)	58	(**12c**)[c)]
$-(CH_2)_2-$		(**7d**)	64	(**11d**)	44	(**12d**)
$-(CH_2)_3-$		(**7e**)	60	(**11e**)	53	(**12e**)
$-(CH_2)_4-$		(**7f**)	51	(**11f**)	54	(**12f**)
$-(CH_2)_5-$		(**7g**)	60	(**11g**)	47	(**12g**)
$-(CH_2)_9-$		(**7h**)	50	(**11h**)	49	(**12h**)

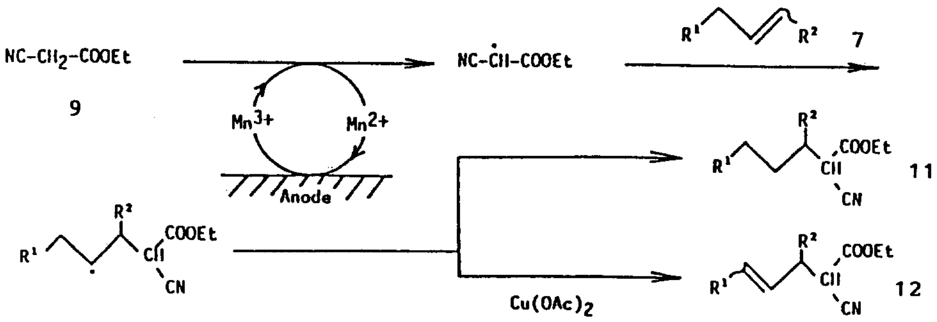
a) Satisfactory spectroscopic analytical results(IR, ^{1}H-NMR, and MS) were obtained for all the products **11a-h** and **12a-h**. b) Isolated yields based on the olefins **7**, which have not been optimized as yet. c) The products **12a-c** were found to consist of a (E)-stereoisomer exclusively.

It is interesting that the present oxidative carbon-carbon bond formation took place regioselectively according to the Markovnikov's rule as shown for the reaction of **7a-c** in Table 2. On the other hand, treatment of a mixture of cis and trans 2-octene(**7i,j**) as an olefin under the similar condition **A** led to the formation of a mixture consisting of 2-octyl and 3-octyl adducts(**11i,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(**12i,j**) in almost the same ratio of 69:31.

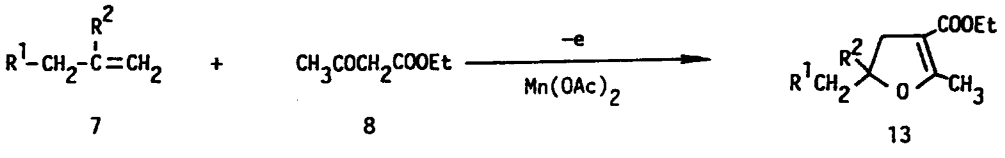


These results may indicate that regioselectivity of the carbon-carbon bond formation of the present electrooxidation is principally attributed to steric effect as well as stability of the intermediates generated in situ. As shown in Table 2, it may be also interesting that only (E)-allylic coupling products, **12a-c** and **12i,j**, were stereoselectively obtained from the reaction of **7a-c** and **7i,j** with **9** under the condition B.

Although a detailed mechanism of the present Mn^{+3}-mediated coupling has been not clear as yet, the following scheme may be proposed as a plausible reaction pathway. A Mn^{+2}-ion may be oxidized electrochemically to an active Mn^{+3}-ion on the anode,9) which has been known to give a methine radical species of ethyl cyanoacetate(**9**) and a Mn^{+2}-ion through formation and thermal decomposition of the corresponding complex.10) Addition of this methine radical to a carbon-carbon double bond of an olefin may generate a new radical intermediate which abstracts a hydrogen atom from the solvent or **9** to form a saturated coupling product **11**. Presence of Cu(OAc)$_2$•H$_2$O may remarkably accelerate further oxidation of the radical intermediate to the corresponding organocopper complex11) followed by β-elimination to give an unsaturated product **12**.



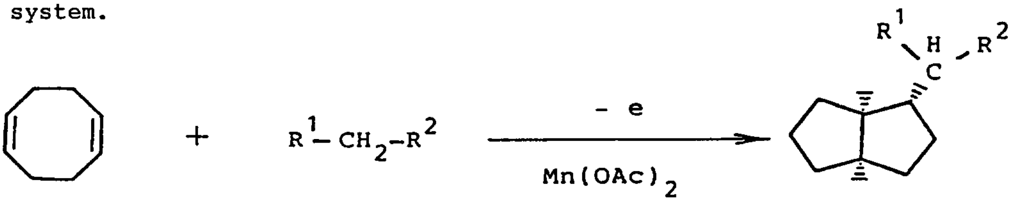
On the other hand, dihydrofuran derivatives(**13**) were obtained in good yields as the single products from Mn^{+3}-mediated anodic coupling of non-activated olefins **7** with ethyl acetoacetate **8** using 0.1 equivalent mole of $Mn(OAc)_2 \cdot 4H_2O$(**2**) under the similar conditions. The similar products were obtained by the reported conventional methods[12] using a stoichiometric amount(2.0 eq.moles) of unstable manganese(III) acetate(**1**).



$R^1 = CH_3CH_2CH_2$, $R^2 = H$ (Y=86%); $R^1 = CH_3(CH_2)_4$, $R^2 = H$ (Y=80%); $R^1 = C(CH_3)_3$, $R^2 = CH_3$ (Y=82%)

3. Mn^{+3}-Mediated Coupling-Cyclization of 1,5-Cyclooctadiene with Active Methylene Compoumnds by Electrooxidation

we have also made further application of the oxidative carbon-carbon bond formation to the similar coupling of unconjugated or conjugated diene systems with active methylene compounds by indirect electro-oxidation in the presence of Mn^{+3}-mediator. Thus, indirect anodic oxidation in a solution containing cycloocta-1,5-diene(**14**),0.2 equivalent mole of $Mn(OAc)_2 \cdot 4H_2O$(**2**), and ethyl cyanoacetate(**9**)(or diethyl malonate (**10**)) brought about selective formation of a coupling-intramolecular cyclization product, ethyl exo-(2-bicyclo[3.3.0]octyl)cyanoacetate (**15**) (or diethyl exo-(2-bicyclo[3.3.0]octyl)malonate (**16**))[13]. The desired coupling products **15** and **16** were obtained in 76% and 78% yields under the optimum conditions at the present stage respectively, through indirect electrooxidation at 20-25 ℃ and 45-50 ℃ in a mixed solvent of acetic acid and ethyl acetate(volume ratio: 65/35) containing triethylamine as a supporting electrolyte, until 3.0 F/mol of electricity passed through the system.



14

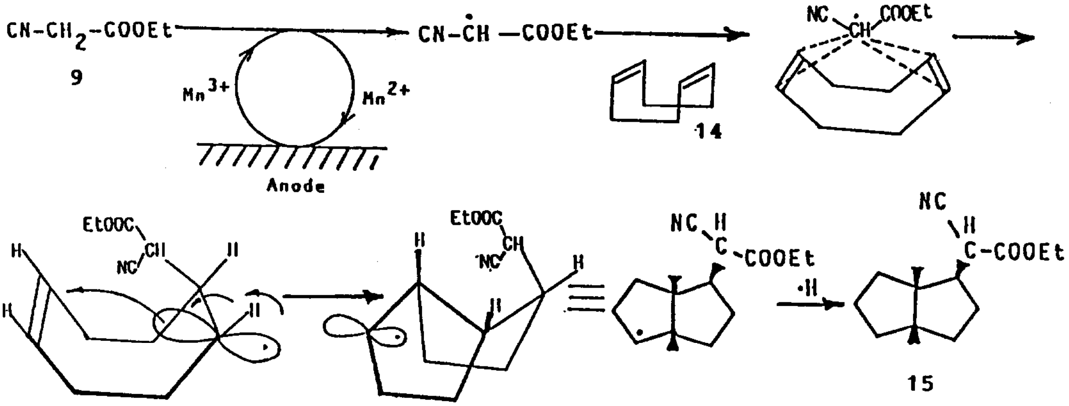
9: R^1=CN, R^2=COOEt
10: R^1= R^2=COOEt

15 [15a (R^1=CN, R^2=COOEt) ; 15b (R^1=COOEt, R^2=CN)] Y : 76%

16 [R^1=R^2=COOEt] Y : 78%

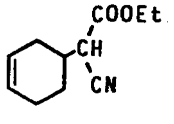
It may be noteworthy that the active methine groups of the product **15** and **16** were found to possess only exo-stereoconfiguration by detailed NMR analysis(see Experimental Section), and the product **15** consisted of two diastereoisomeric mixtures, **15a,b**(ratio: ca.1:1).

The following reaction pathway may be proposed in order to explain the present stereoselective formation of the cyclized coupling products 15 and 16.

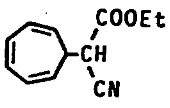


Radical species of active methylene compounds **9** and **10** formed from electrogenerated Mn^{+3}-ion as described before[9),10)] may make "inside attack" to a carbon-carbon double bond of the folded-type conformation of 1,5-cyclooctadiene (**14**) to give a new radical intermediate. Interaction of this radical with the other carbon-carbon double bond may afford cyclized radical species, in which two bridgehead hydrogen atoms are oriented to the same direction as the active methine groups.[14)]

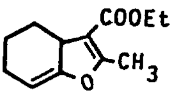
Treatment of 1,4-cyclohexadiene and 1,3,5-cycloheptatriene under the similar conditions resulted in formation of simple coupling products, namely ethyl (cyclohex-3-enyl)cyanoacetate(**17**) and ethyl (2-cycloheptatrienyl)cyanoacetate (**18**), in 47 and 52% yields, respectively.



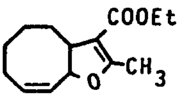
17
Yield = 47%



18
Yield = 52%



19a
Yield = 43%



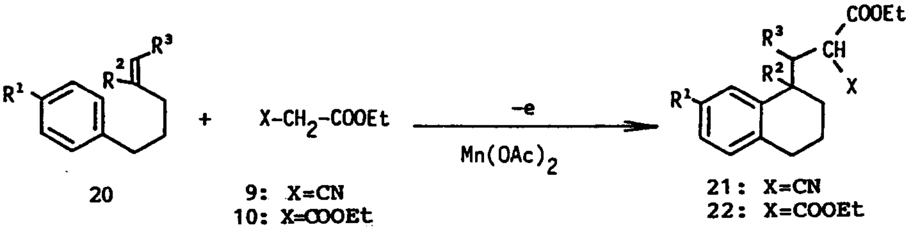
19b
Yield = 41%

Employment of ethyl acetoacetate(8) as an active methylene compound in the present Mn^{+3}-mediated coupling of conjugated dienes such as cyclohexa-1,3-diene and cycloocta-1,3-diene by electrooxidation led to selective formation of the corresponding dihydrofuran derivatives **19a,b**, in moderate yields, as was observed in the similar oxidative coupling reaction of nonactivated monoolefins.

4.Mn^{+3}-Mediated Coupling-Cyclization of 5-Arylpent-1-enes with Active Methylene Compounds by Electrooxidation.

Alternatively, specific cyclized products, 1-(2,2-disubstituted) ethyltetralines (**21a-e**) and (**22a-e**), were selectively obtained in good to moderate yields from the similar Mn^{+3}-mediated coupling of 5-arylpent-1-enes(**20a-e**) with active methylene compounds **9** and **10** by electrooxidation under the similar conditions, as shown in Table 3.

Table 3. Mn^{+3}-Mediated Coupling-Cyclization of 5-Arylpent-1-enes with Active Methylene Compounds by Electrooxidation .



20

9: X=CN
10: X=COOEt

21: X=CN
22: X=COOEt

5-Arylpent-1-enes				Isolated Yield(%) of Products			
R^1	R^2	R^3		X = CN		X = COOEt	
H	H	H	(20a)	70	(21a)	79	(22a)
Me	H	H	(20b)	58	(21b)	61	(22b)
F	H	H	(20c)	53	(21c)	60	(22c)
H	Me	H	(20d)	60	(21d)	73	(22d)
H	H	Me	(20e)	37	(21e)	39	(22e)

The lower yields of the products **21e** and **22e** may be attributed to steric hindrance on addition of the radical species generated from active methylene compounds **9** and **10** to the carbon-carbon double bond of **20e**. Isolated yields of the products **21b** and **22b** having a methyl group on their phenyl ring were almost the same as those of **21c** and **22c** having a fluoro group. This phenomenon indicates that cyclization proceeds through a radical mechanism.

Experimental Section

Typical Procedure for Carboxymethylation of Styrene Derivatives (3) to γ-Aryl-γ-Butyrolactones(4): The electrolysis apparatus was a divided cell equipped with a ceramic cylinder as a diaphragm and carbon rods as anode and cathode, and the cathodic and anodic chambers were 120 and 30 ml, respectively. A mixed solvent of glacial acetic acid(50 ml) and acetic anhydride(25 ml) containing 5.0 g(61 mmol) of NaOAc as a supporting electrolyte was placed in the anodic and cathodic chambers, and 9.36 g(90 mmol) of styrene(**3a**), 1.42 g(5.8 mmol) of $Mn(OAc)_2 \cdot 4H_2O$ and 0.44 g(2.2 mmol) of $Cu(OAc)_2 \cdot H_2O$ were added to the anolyte. Stirred with a magnetic bar and heated at 95-97 °C with an oil bath, the electrolysis was carried out under constant-current conditions(current density: 1.0 A/dm^2) until 36 mF of electricity, corresponding to a theoretical amount of electricity(2.0 F/mol) for oxidative transformation of 18 mmol of **3a** to γ-phenyl-γ-butyrolactone(**4a**), passed through the system. After the reaction, the anolyte was poured into 250 ml of aqueous saturated NaCl solution and extracted with three 100-ml portions of ethyl ether. The combined ethereal solution was neutralized with aqueous saturated $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. After filtration of the drying agent and evaporation of the solvent, the residue was distilled in vacuo to give 2.33 g (current yield(C.E.): 80 %) of γ-phenyl-γ-butyrolactone (**4a**) as the main product accompanying 0.32 g (C.E.: 8 %) of α,β-diacetoxyethylbenzene(**5a**) as a by-product.

γ-Phenyl-γ-butyrolactone(4a): bp 155-158 °C/3mm (Lit.[15] 130 °C/1.5 mm)

Typical Procedure for Carbon-Carbon Bond Formation between Non-Activated Olefins(7) and Active Methylene Compounds(8-10) by Mn^{+3}-Mediated Electro-oxidation (Condition A)

A solution of 4.92 g(60 mmol) of NaOAc in 80 ml of a mixed solvent of glacial acetic acid and ethyl acetate (volume ratio: 13:3) was placed in anodic and cathodic chambers of a similar divided cell to described above. To the anolyte were added 0.49 g(2.0 mmol) of $Mn(OAc)_2 \cdot 4H_2O$, 0.82 g (10 mmol) of cyclohexene(**7e**) and 3.39 g(30 mmol) of ethyl cyanoacetate(**9**). (Under the condition B, 0.10 g(1.0 mmol) of $Cu(OAc)_2 \cdot H_2O$ was also added.) The electrolysis was carried out under constant-current conditions(current density: 2.0 A/dm^2) at 40 °C with magnetic stirring until 2.0 F/mol of electricity based on **7e** passed through the system. The same usual work-up of the anolyte, as described above, followed by column chromatography of the crude mixture over silica gel(n-C_6H_{14}/EtOAc = 9/1) afforded ethyl cyclohexylcyanoacetate(**11e**) as a sole product in a 60% yield(1.17 g) based on **7e**. (Under the condition B, ethyl (2-cyclohexenyl)cyanoacetate(**12e**) was obtained as the main product in a 53% yield accompanying only trace amount of **11e**.)

Ethyl Cyclohexylcyanoacetate(11e): bp 107-108 °C/3 mm (Lit.[16] 138-139 °C /8 mm)

Ethyl (2-Cyclohexenyl)cyanoacetate(12e): bp 114-115 °C/3.5 mm. IR(neat): 2950, 2250, 1745 cm^{-1}. ^1H-NMR(270 MHz, $CDCl_3$, ppm) δ 1.33(3H, t, J=7.0 Hz), 3.42(1H, d, J=6.0 Hz), 3.49(1H, d, J=6.0 Hz), 4.28(2H, q, J=7.0 Hz), 5.47(1H, dq, J=10.5 & 1.0 Hz), 5.60(1H, dq, J=10.5 & 1.0 Hz), 5.94(2H, br d, J=10. 5 Hz). HR-MASS: for $C_{11}H_{15}O_2N$, m/e Calcd; 193.1103, Found; 193.1068.

Typical Procedure for Mn^{+3}-Mediated Coupling-Cyclization of 1,5-Cyclooctadiene(14) with Active Methylene Compounds(9,10) by Electrooxidation

Into anodic and cathodic chambers of the same divided cell as employed before was introduced a solution of 65 ml of glacial acetic acid and 35 ml of ethyl acetate containing 6.15 g(60 mmol) of triethylamine as a supporting electrolyte, and 1.08 (10 mmol) of 1,5-cyclooctadiene(**14**), 3.39 g(30 mmol) of ethyl cyanoacetate(**9**)(or 4.80 g(30 mmol) of diethyl malonate(**10**)) and 0.49 g of $Mn(OAc)_2 \cdot 4H_2O$ were added into the anolyte.

Stirred with a magnetic bar, the anolyte was electrochemically oxidized at room temperature(20-25 ^{0}C) under constant-current conditions(current density: 2.0 A/dm^{2}). After 3.0 F/mol of electricity based on **14** passed through the reaction system, the anolyte was worked-up according to the usual procedure to give 1.67 g (yield: 76%) of ethyl exo-(2-bicyclo[3.3.0] octyl)cyanoacetate(**15**)(or 2.09 g(yield: 78%) of diethyl exo-(2-bicyclo-[3.3.0]octyl)malonate(**16**)) as a sole product. The ^{13}C-NMR spectrum of **15** showed 13 pairs of carbon-signals indicating that **15** consists of almost even ratio of the corresponding diastereomers while only 13 carbon-signals were observed for that of **16**.

Ethyl Exo-(2-bicyclo[3.3.0]octyl)cyanoacetate(15): bp 128-129 ^{0}C/3mm IR(neat): 2950, 2875, 2260, 1740, 1035 cm^{-1}. ^{1}H-NMR(270 MHz,CDCl$_3$, ppm) :δ 1.32 (3H, t, J=7.0 Hz), 3.57(1H, t, J=6.0 Hz), 4.25(2H, q, J=7.0 Hz). ^{13}C-NMR (270 MHz, CDCl$_3$, ppm)δ 13.74, 25.00, 25.32, 31.25, 31.74, 32.23, 32.32, 32.56, 32.69, 32.78, 32.89, 32.94, 41.79, 42.12, 43.17, 43.81, 46.77, 47.23, 47.42, 47.46, 62.19, 66.25, 115.67, 115.86, 165.85, 165.94. HR-MASS: for $C_{13}H_{19}O_2N$ m/e Calcd; 221.1416, Found; 221.1406.

Diethyl Exo-(2-bicyclo[3.3.0.]octyl)malonate(16): bp 108-109 ^{0}C/2.5mm IR(neat): 2950, 2850, 1750, 1725 cm^{-1}. 1H-NMR(270 MHz, CDCl$_3$, ppm):δ 1.26(3H, t, J=7.0 Hz), 1.27(3H, t, J=7.0 Hz), 3.21(1H, d, J=9.0 Hz), 4.18 (4H, q, J=7.0 Hz). ^{13}C-NMR(270 MHz, CDCl$_3$, ppm):δ 14.07, 25.77, 31.02, 32.58, 33.01, 33.27, 43.72, 46.96, 47.54, 57.01, 61.00, 61.06, 168.90, 169.03. HR-MASS: for $C_{15}H_{24}O_4$ m/e Calcd; 268.1675, Found; 268.1703.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas(No. 01607001)from Ministry of Education, Science and Culture of Japan.

References and Notes

1)Author to whom correspondence should be addressed at Osaka Municipal Technical Research Institute.

2)W.J.Mijs and C.R.H.I.de Jonge, eds., "Organic Synthesis by Oxidation with Metal Compounds", pp 261-314, Plenume Press, New York(1986).

3)a)W.E.Fristad and J.R.Peterson, J.Org.Chem., **50**, 10(1985): b)F.Viebock, Chem. Ber., **67**, 197(1934): c)S.A.Zonis and Sb.Statei, Obshch. Khim., **2**, 1091(1953); Chem. Abstr., **49**, 5414q(1955).

4)Similar Mn^{+3}-mediated electrochemical lactonization of 1,3-butadiene was shown in patents by a Monsanto Group. See Monsanto, **USP** 4,526,990, (1985), 4,560,775(1986), 4,564,689(1986).

5)a)J.B.Bush and H.Finkbeiner, J.Am.Chem.Soc.,**90**, 5904(1968): b)E.I.Heiba, R.M.Dessau, and W.J.Koehl, ibid, **90**, 5906(1968)

6)R.Shundo,I.Nishiguchi,Y.Matsubara,T.Hirashima, to be published

7)a)W.J. de Klein, Recueil. J. Royal Neth. Chem. Soc., **94**, 48(1975): b)P.Boldt and H.Militzer, Tetrahedron Lett., **1966**, 3599: c)J. Yoshida, K. Sakaguchi,and S.Isoe, Tetrahedron Lett., **1987**, 667:d)S.Torii,K. Uneyama, T.Onishi,Y.Fujita,M.Ishiguro,and T.Nishida,Chem.Lett.,**1980**, 1603: e)H. Schafer and A.Alazrah, Angew.Chem.Int.Ed.Engl., **7**, 474(1968).

8)H.O.House,"Modern Synthetic Reactions", 2nd ed., pp 595-623, W.A.Benjamin Inc., Menlo Park USA(1972).

9)The redox potential of the couple Mn^{+3}/Mn^{+2} was reported to be 1.04 V vs. NHE. See R.U.G.Khirishnam,R.V.Venka,B.Sethuram, and R.Naraneeth, J. Electroanal. Chem., **133**, 1103(1982).

10)a)A.Citterio,D.Francelli,C.Finzi,and L.Pesce, J. Org. Chem., **54**, 2713 (1989):b)A.Citterio,R.Santi,T.Fiorani,and S.Strologo,ibid.,**54**, 2703(1989)

11)M.A.Dombroski and B.B.Snider, Tetrahedron Lett., **1987**, 845.

12)E.I.Heiba, and R.M.Dessau, J.Org.Chem., **39**. 3456(1974)

13)Recently Mn^{+3}-based oxidative intramolecular cyclizations have been extensively studied. See M.A.Dombroski, S.A.Kates, and B.B.Snider, J. Am. Chem. Soc., **112**, 2759(1990), and others cited therein.

14)a)R.Dowbenko, Tetrahedron, **20**, 1843(1964):b)I.Tabushi,K.Fujit, and R. Oda, J.Org.Chem., 35, 2376(1970).

15)V.Russel and R.Vanderwerf, J.Am.Chem.Soc.,**69**, 11(1947).

16)E.R.Alliot and A.C.Cope, J.Am.Chem.Soc., **66**, 886(1944).