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

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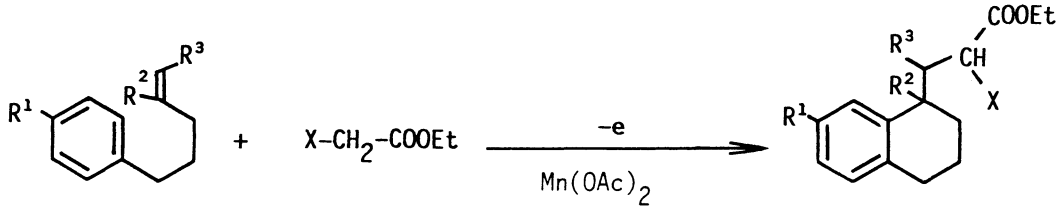
Selective coupling-cyclization of 5-arylpent-1-enes with active methylene compounds was developed by indirect electrooxidation using a small amount of $Mn(OAc)_2 \cdot 4H_2O$ to give 1-[2,2-(disubstituted)ethyl]tetralines in good yields.

Much attention has been focused on tetraline synthesis by free-radical cyclization[1)] because of much usefulness and high potentiality of tetraline derivatives for synthesis of some of pharmaceutical drugs.[2)]

In this communication, we wish to present Mn^{3+}-mediated coupling-cyclization of 5-arylpent-1-enes with active methylene compounds by indirect electrooxidation using *in situ* generation[3)] of the active Mn^{3+}-ion from a small amount of $Mn(OAc)_2 \cdot 4H_2O$ and its recycle use, to give selectively the corresponding 1-[2,2-(disubstituted)ethyl]tetralines **4**, **5**.[4)]



2: X=CN
3: X=COOEt

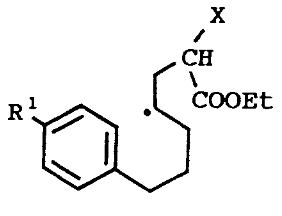
4: X=CN
5: X=COOEt

The typical procedure is as follows : A solution of 4.92 g (60 mmol) of NaOAc in 80 ml of a mixed solvent of AcOH and AcOEt (volume ratio 13:3) was placed in an anodic and a 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 $Mn(OAc)_2.4H_2O$, 1.49 g (10 mmol) of 5-phenyl-pent-1-ene (**1a**) and 4.80 g (30 mmol) of diethyl malonate (**3**). The electrolysis was carried out under constant-current conditions (current density : 2.0-3.0 A/dm^2) at 60 °C until 2 F/mol of electricity based on **1a** was passed through the system. The usual work-up followed by column chromatography of the crude product mixture over silica gel (hexane/EtOAc=9/1) afforded 1-[2,2-bis(ethoxycarbonyl)ethyl]tetraline (**5a**) in a 79% yield (2.40 g) based on **1a**. A variety of 1-[2,2-(disubstituted)ethyl]tetralines **4**, **5** were also obtained in moderate to good yields from the similar Mn^{3+}-mediated anodic coupling-cyclization of the corresponding 5-aryl-pent-1-enes **1** with ethyl cyanoacetate (**2**) and diethyl malonate (**3**), as shown in Table 1.

Table 1. Mn^{3+}-Mediated Anodic Coupling-Cyclization of 5-Arylpent-1-enes (**1**) with Active Methylene Compounds **2**, **3** by Electrooxidation

5-Arylpent-1-enes				Isolated yield/% of products			
R^1	R^2	R^3		X=CN		X=COOEt	
H	H	H	(**1a**)	70	(**4a**)	79	(**5a**)
Me	H	H	(**1b**)	58	(**4b**)	61	(**5b**)
F	H	H	(**1c**)	53	(**4c**)	60	(**5c**)
H	Me	H	(**1d**)	60	(**4d**)	73	(**5d**)
H	H	Me	(**1e**)	37	(**4e**)	39	(**5e**)

The lower yields of the products **4e** and **5e** may be attributed to steric hindrance on addition of the radical species$^{5)}$ generated from active methylene compounds **2** and **3** to the carbon-carbon double bond of **1e**. Isolated yields of the products **4b** and **5b** having a methyl group on their phenyl rings were almost the same as those of **4c** and **5c** having a fluoro group. This phenomenon may indicate that the reaction proceeds through intramolecular radical cyclization of the generated intermediate **6**.



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References
1) E. I. Heiba and R. M. Dessau, J. Am. Chem. Soc., 94, 2888 (1972).
2) D. Lednicer and L. A. Mitscher, "The Organic Chemistry of Drug Synthesis," Wiley-Interscience Publication, New York (1977), pp. 145-217.
3) The redox potential of the couple Mn(III)/Mn(II) 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).
4) Recently Mn^{3+}-mediated carboxymethylation of butadiene was reported in patents. See, Monsanto, U. S. Patent, 4526990, 4560775, 4564689 (1986).
5) R. Shundo, I. Nishiguchi, Y. Matsubara, and T. Hirashima, Chem. Lett., in press.

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