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Electrochemical Wacker Type Reaction with a Double Mediatory System Consisting of Palladium Complex and Tri(4-bromophenyl)amine

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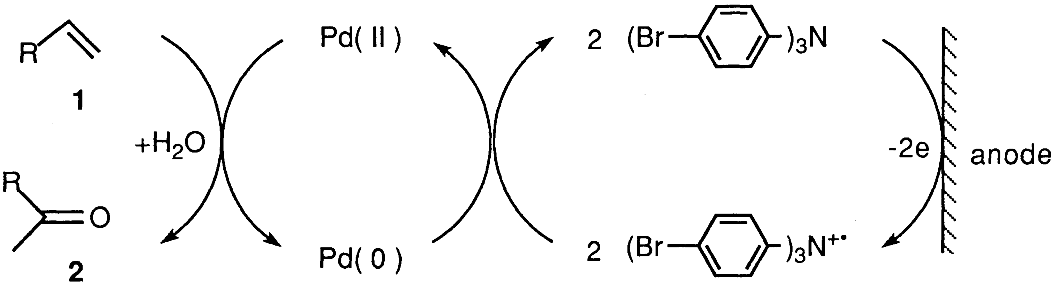
The electrochemical Wacker type oxidation of terminal olefins by using palladium chloride or palladium acetate and tri(4-bromophenyl)amine as a recyclable mediator in either a divided cell or an undivided cell afforded the corressponding methyl ketones in good yields.

The Wacker type process with palladium(II) chloride and copper(II) as catalysts in aqueous media under oxygen is one of the useful methods for conversion of terminal olefins to methyl ketones.[1)] A variety of modified methods of this reaction by devising the reoxidation process for palladium(0) to palladium(II) have been reported in order to avoid chlorination encountered in the process with copper(II) chloride.[2)] Electrooxidation methods were also employed for the direct oxidation of Pd(0) to Pd(II)[3)] or for generation of recyclable oxidants such as quinone[4)] or ferric chloride[5)] as a co-oxidant for regeneration of Pd(II) catalyst. Usually divided cell systems have been utilized to avoid the deposition of palladium metal onto the cathode, which often led to unsatisfactory reaction conversion.[6)] Herein, we report an improved procedure for the electrochemical Wacker type reaction by use of triarylamine as a recyclable mediator[7)] for regeneration of Pd(II) from Pd(0). The electrolysis can be achieved in both a divided or an undivided cells. In this double mediatory system, electrooxidation effects formation of triarylamine cation radical from triarylamine which regenerates palladium(II) species.



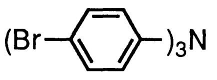
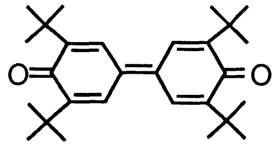
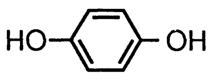
The cation radicals of triarylamines are stable[8)] and hence useful as redox catalysts for indirect electrooxidations such as deprotonation and irreversible cleavage of carbon-sulfur bond.[7)] Redox step by the cation radical of triarylamine is considered to involve the formation of an intermediate complex, which would lead to a negative shift of the oxidation potential compared with those of the substrates.[9)] These features of the cation radicals of triarylamines are of interest as a recyclable organic redox for regeneration of Pd(II) from Pd(0) in the double mediatory system.

The electrolyses were carried out either in a divided or undivided cell under a constant applied voltage. Typically, the electrolysis in an undivided cell was performed by using the substrate (1 mmol), $PdCl_2$ (5 mol%), and $(4\text{-}BrC_6H_4)_3N$ (5 mol%) in an $MeCN\text{-}H_2O$ (7:1)-(Pt)-(Pt) system at an applied voltage of 3 V, current 2–3 mA for 2–3F/mol, giving the desired methyl ketones. The results of the electrochemical Wacker oxidations are given in Table 2.

In our attempt to find out the most favorable organic mediator for the electrochemical process in the double mediatory system, three kinds of organic redoxes such as triarylamine **3**, diphenoquinone **4** and hydroquinone **5** were examined for the oxidation of 1-undencene (**1a**). It is known that in general unsubstituted terminal olefins like **1a** are susceptible to the isomerization of double bond to internal positions during the palladium-catalyzed Wacker process. As shown in Table 1, the ratio of the desired 2-undecane (**2a**) vs other ketones such as 3-, and 4- and 5-undecanones is affected by the kind of organic mediator. Among three organic mediators attempted, the highest yield of the Wacker oxidation product and the highest product selectivity of **2a** are observed with tri(4-bromophenyl)amine (**3**).

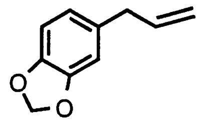
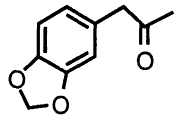
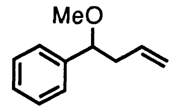
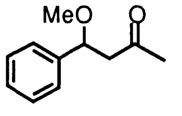
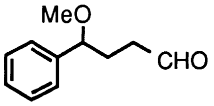
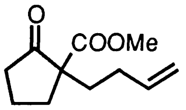
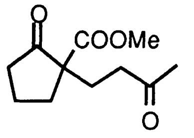
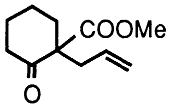
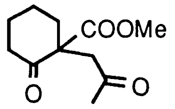
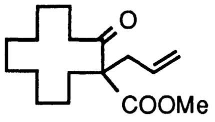
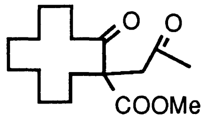
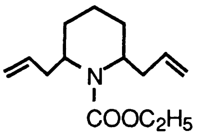
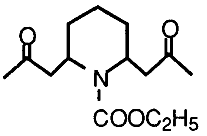
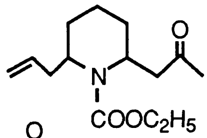
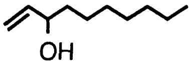
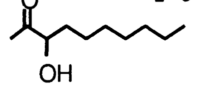
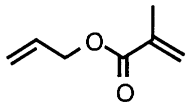
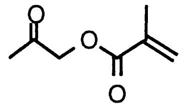
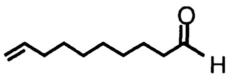
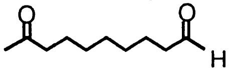
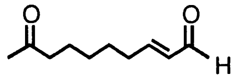
The efficiency of the electrooxidation is also affected by the kind of palladium complexes. $PdCl_2$ and $Pd(OAc)_2$ were preferentially used in the undivided and divided cell systems, respectively.

Table 1. Electrochemical Wacker Oxidation of 1-Undecene (**1a**) with Organic Mediators[a)]

Entry	Organic mediators		Products/Yield/ %		Total
			2a[b)]	Other ketones[c)]	yield/%[d)]
1		**3**	39 (43)	51 (57)	90
2		**4**	30 (39)	46 (61)	76
3		**5**	27 (31)	51 (69)	88

a) Reaction is carried out in a CH_3CN/H_2O (9:1 V/V, 10 ml)-Et_4NOTs- (Pt)-(Pt) system in the presence of $Pd(OAc)_2$ (5 mol%) and an organic mediator (20 mol%) at room temperature (20 °C) in a divided cell. Conditions: 3.0 V (0.4–5.5 mA); Electricity charged: 2.5–3.0 F/mol. b) Yields are determined by GC analyses based on internal standard (2-octanone). Numbers in a parenthesis show selectivity of **2a**. c) Combined yield of 3-, 4-, and 5-undecanones by GC analyses. Numbers in a parenthesis show selectivity of these ketones. d) Combined yield of **2a** and other ketones. Yields are determined by GC analyses.

Table 2. Electrochemical Wacker Process with a Combination of $Pd(OAc)_2$ or $PdCl_2$ and $(4\text{-}BrC_6H_4)_3N$ in a Divided or an Undivided Cell[a]

Entry	Substrates **1**		Products		Yield/%[b]	
					Divided cell	Undivided cell
1		**b**		**2b**	57	85
2		**c**		**2c**	82	89
				**6**	10	-
3		**d**		**2d**	89	60
4		**e**		**2e**	93	90
5		**f**		**2f**	79	48
6		**g**		**2g**	74	72
				**7**	16	-
7		**h**		**2h**	70	41
8		**i**		**2i**	64	66
9		**j**		**2j**	46	74
				**8**	22	4

a) Reaction is carried out by using substrates **1** (1 mmol) and $Pd(OAc)_2$ (divided) or $PdCl_2$ (undivided) (0.05 mmol) in an $MeCN\text{-}H_2O$ (7:1)-0.5 M Et_4NOTs-(Pt)-(Pt) system at room temperature for 2.0—3.0 F/mol of electricity. b) Yields based on isolated products.

The combined use of $PdCl_2$ or $Pd(OAc)_2$ palladium chloride or palladium acetate with tri(4-bromophenyl)amine (**3**) was applied to the oxidation of a variety of terminal olefins and the results are shown in Table 2. The desired methyl ketones **2** are obtained in good yields when the starting olefins possess substituents such as a methoxy group (Entry 2), carbonyl functions (Entries 3-5) and an amino group (Entry 6) at the neighboring positions. A small amount of by-products such as aldehdye (Entry 2) and dehydrated compound (Entry 9) are found. Up to 50 turnover of the palladium catalyst could be achieved without noticeable loss of activity of the electrolysis system.

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