

Note

The electrosynthesis of pinacols

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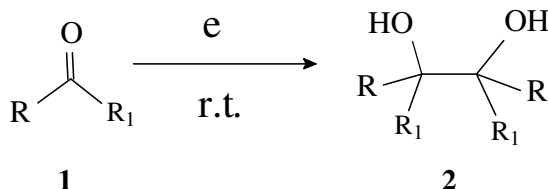
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Electrosynthesis of pinacols by iron as electrode in acid condition is performed. The influence of electric potential and time on pinacol yield is explored. The optimal reaction conditions are at electric potential 4 V, time 60 min., methanol (6 mL), hydrochloric acid (2 N, 2 mL), with the yield of pinacols up to 18-81%. The main advantages of the present procedure are milder reaction conditions and operational simplicity.

Keywords: Pinacols, electrosynthesis, iron, electrode, aqueous

1,2-Diols are very useful synthons for a variety of organic syntheses¹, and which have been used as intermediates for the construction of biologically important natural product skeletons². In the last few years, several metals such as Mg³, Mn⁴, Al⁵, In⁶, transition metal^{7, 8} and rare earth metal⁹ have been reported to mediate the pinacol coupling reaction. However, some of the reduction conditions are critical and are often associated with the toxic heavy metals, which would lead to economical and environmental concerns.

Electrosynthesis has increasingly been used in organic synthesis. Recently, some researches have been reported for electrosynthesis promoted pinacol coupling of aromatic aldehydes by using Sn¹⁰, Cd¹¹, Zn-PTFE^{12,13}. A search of the literature revealed that no work had been reported on the pinacol coupling reactions using iron as electrode in aqueous media to date. Herein, the results of the pinacol coupling reactions of aromatic aldehydes in aqueous media by Fe as electrode (**Scheme I** and **Table I**) is reported.



Scheme I

Table I—Optimization of pinacol of C₆H₅CHO in acidic aqueous media using Fe as electrode

Entry	C ₆ H ₅ CHO (g)	Electric potential (V)	Time min	Methanol /mL	HCl mole /L	Yield (%)
1	0.1217	2	60	6	2	11.4
2	0.1217	3	60	6	2	57.7
3	0.1217	4	60	6	2	81
4	0.1217	5	60	6	2	75.1
5	0.1217	4	60	6	1	51
6	0.1217	4	60	6	2	81
7	0.1217	4	60	6	3	80
8	0.1217	4	60	6	4	72.5
9	0.1217	4	20	6	2	22.5
10	0.1217	4	40	6	2	61.2
11	0.1217	4	60	6	2	81
12	0.1217	4	80	6	2	79.1

Several experiments were carried out taking benzaldehyde as substrate and varying the electric potential, the amount of hydrochloric acid and reaction time using electrosynthesis and the results are given in **Table I**. As can be seen from **Table I**, the electric potential has also significant effect on the reaction yield, when the electric potential varied from 2 V to 4 V, the yield of pinacol also increased from 11.4 to 81%. Prolonging the reaction time from 20 min. to 60 min., the yield of pinacol increased from 22.5 to 81%. When the amount of hydrochloric acid was increased from 1 mL to 2 mL, the yield of pinacol increased from 51 to 81%. So the reaction conditions chosen were: C₆H₅CHO (1 mmole), electric potential 4 V, time 60 min., methanol (6 mL), hydrochloric acid (2 N) 2 mL.

A series of experiments were carried out with the above reaction system for pinacol coupling of aromatic aldehydes using electrosynthesis. As shown in **Table II**, a number of aromatic aldehydes underwent pinacol coupling to give pinacols in moderate to good yields in acidic aqueous media using electrosynthesis. For example, with the substrates **1a**, **1b**, **1c** and **1d**, the corresponding pinacol product were obtained in 81, 75, 69 and 70% yield respectively, after 60 min. of the electro-irradiation: Whereas in the same system, the yields of pinacol (**2e** and **2f**) were 18, 48% respectively, after 60 min. When ketones were used as substrates, no

pinacols were obtained, Which showed that the steric hindrance around the carbonyl group might inhibit the pinacol coupling reactions.

It is well-known^{2,7} that pinacol coupling proceeds via a single electron-transfer mechanism. An alternative and often competing reaction to pinacolization is the reduction of carbonyl to the corresponding alcohol. In the present process, pinacol was found to be the sole product. Coupling is propagated by single-electron reduction of the carbonyl group to form a ketyl radical anion **I**, which either undergone radical-radical coupling (route a), or was further reduced to the corresponding dianion **II** and then nucleophilically attacked a second carbonyl group (route b), leading to pinacol formation (**Figure 1**), while dianion **II** could be protonated by H^+ to give alcohol as a major product. Electro-irradiation as an energy source could promote generation of the radicals and initiate the electron transfer process.

In summary, a rapid, economical and environmental friendly approach for the preparation of pinacols using iron as electrode is developed. The

main advantage of the present procedure is the mild reaction conditions and simplicity of operation. More importantly, there is no single alcohols obtained, so this new approach shows the considerable practical value due to its efficiency and simplicity.

Experimental Section

Liquid substrates were distilled before use. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). MS spectra were measured on an AEI MS-50 SD90 spectrometer (EI, 70 eV). 1H NMR spectra were measured on a VXR-300S spectrometer (300 MHz) with $CDCl_3$ as solvent and TMS as internal standard. Electrosynthesis was performed in a Shanghai 31-V0.045-600W direct-current voltmeter (Shanghai secondary instrument plant).

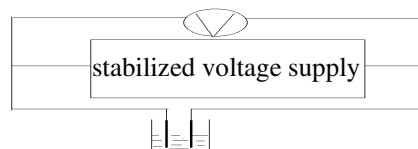
General procedure

Typical method: In a 50-mL beaker fitted with two Fe plates as the anode and the cathode (4 cm \times 8 cm), the distance between the anode and the cathode is 2.5 cm, methanol (6 mL) was introduced as the solvent and hydrochloric acid (2 mole/L, 2 mL) as supporting electrolyte, then the corresponding aldehyde or ketone (**1**, 1 mmole) was added, the mixture was electrolysed at 25-30°C for 1 hr. After completion of the reaction, the filtrate was extracted with ethyl acetate (3 \times 10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and

Table II — Pinacol coupling of aromatic aldehydes in aqueous media using Fe as electrode

Entry	Substrate	Isolated yield (%)	<i>dl/meso</i> *
a	C_6H_5CHO	81	48/52
b	$4-ClC_6H_4CHO$	75	60/40
c	furfural	69	meso
d	cinnamaldehyde	70	56/44
e	$3,4-(OCH_2O)C_6H_3CHO$	18	36/64
f	$4-CH_3OC_6H_4CHO$	48	38/62
g	$C_6H_5COC_6H_5$	0	-
h	$C_6H_5COCH_3$	0	-

*Ratio of *dl/meso* was determined by 1H NMR; electrolysis time for 1 hr.



Reaction device

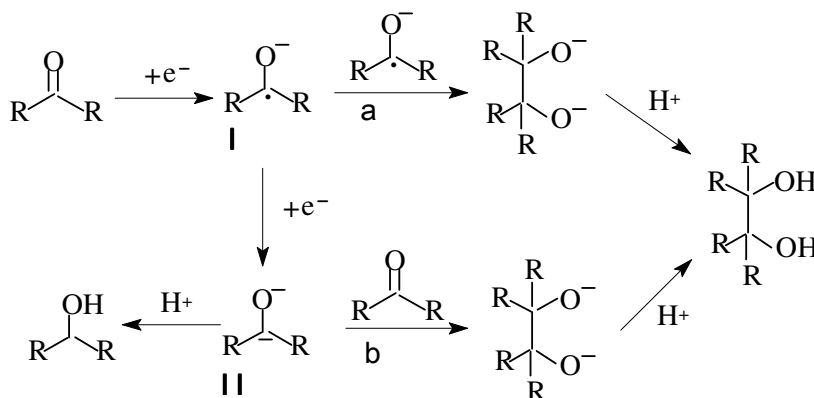


Figure 1 — Mechanism for the pinacol coupling of aromatic aldehydes by electrosynthesis

brine, dried over anhydrous magnesium sulfate for 12 hr and filtered. Ethyl acetate was evaporated under reduced pressure to give the crude product, which was separated by column chromatography on silica (200-300 mesh), eluted with petroleum ether or a mixture of petroleum ether and diethyl ether. All the products were confirmed by IR, MS, ^1H NMR spectral data.

2a ^1H NMR: δ 2.30 (s, 2H, OH), 4.80 (s, dl), 4.88 (s, *meso*), (2H, PhCH-), 7.16-7.32 (m, 10H, Ar); m/z (%): 214 (1), 180 (7.6), 167 (12.5), 149 (6.0), 107 (93.8), 79 (100), 77 (73.8); IR (KBr): 3490 (br) cm^{-1} .

2b ^1H NMR: δ 2.34 (s, 2H, OH), 4.66 (s, dl), 4.88 (s, *meso*), (2H, PhCH-), 7.06-7.32 (m, 8H, Ar); m/z (%): 284(1), 282 (10), 235 (12), 165 (5.5), 141 (100), 107 (19), 77 (10); IR (KBr): 3400 (br) cm^{-1} .

2c ^1H NMR: δ 2.08 (s, 2H, -OH), 5.09 (s, dl), 5.12 (s, *meso*), (2H, fur-CH-), 6.30-6.41 (m, 2H, 3,4-fur-H), 7.29 (m, 1H, 5-fur-H); m/z (%): 194 (1), 178 (25), 152 (73), 137 (33), 98 (100), 84 (22), 49 (30); IR (KBr): 3270 (br) cm^{-1} .

2d ^1H NMR: δ 1.89 (s, 2H, OH), 4.49 (s, *meso*), (2H, -CH-OH), 6.39 (t, 2H, -CH=CH-), 6.75 (d, 2H, -CH=CH-), 7.06-7.22 (m, 10H, Ar); m/z (%): 266 (1), 221 (12), 177 (24), 162 (26), 151 (30), 135 (23), 120 (70), 85 (38), 77 (17), 57 (90); IR (KBr): 3410 (br) cm^{-1} .

2e ^1H NMR: δ 2.22 (s, 2H, OH), 5.58 (s, dl), 5.76 (s, *meso*), (2H, PhCH-), 5.94 (s, 4H, -CH₂-), 6.68-6.79 (m, 6H, Ar); m/z (%): 302 (1), 284 (2.5), 268 (5.0), 255 (11.8), 151 (100), 123 (32), 93 (77.1), 65 (39.0); IR (KBr): 3470 (br) cm^{-1} .

2f ^1H NMR: δ 2.98 (s, 2H, OH), 3.72 (s, dl), 3.80 (s, *meso*), (s, 6H, OCH₃), 4.66 (s, dl), 4.76 (s, *meso*), (2H, PhCH-), 6.88-7.28 (m, 8H, Ar); m/z (%): 274(1), 256 (2), 227 (30), 137 (100), 109 (9), 77 (8); IR (KBr): 3340 (br) cm^{-1} .

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