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Reductive Coupling of Carbonyl Compounds to Pinacols with Zinc in *THF*-Saturated Aqueous Ammonium Chloride

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Summary. In the presence of metallic zinc, aldehydes and ketones experience reductive coupling in tetrahydrofuran-saturated aqueous ammonium chloride (5:3) to afford the corresponding pinacols in moderate to high yields.

Keywords. Carbonyl compounds; Pinacols; Zinc; Pinacolization; Carbon-carbon bond formation.

Introduction

The reductive coupling of carbonyl compounds to pinacols constitutes an important method for the formation of vicinally functionalized carbon-carbon bonds [1]. This reaction proceeds by dimerization of carbonyl radical anions formed by single electron transfer from a variety of metals, metal salts, or metal complexes under various conditions. There is a considerable variety of pinacolization procedures [2–8] reflecting the continuous search for more efficiency and higher selectivity.

Results and Discussion

Recently, there has been considerable interest in performing organic reactions in aqueous media [9–11]. We report here that reductive coupling of aldehydes and ketones can be affected easily in tetrahydrofuran and saturated aqueous ammonium chloride in the presence of zinc to afford the corresponding pinacolic alcohols in moderate to fairly high yields. Our results are summarized in Table 1.

Stirring of a mixture of an aldehyde or ketone and zinc powder in *THF*-saturated aqueous ammonium chloride proceeded smoothly at room temperature to give the corresponding pinacols. The procedure was applied to benzaldehydes and cinnamaldehyde as well as cyclohexanone, benzophenone, flourenone, anthrone, xanthone, and thioxanthone (Table 1). The reactions were in most cases completed within 10–50 minutes as evidenced by disappearance of the metal. As shown in

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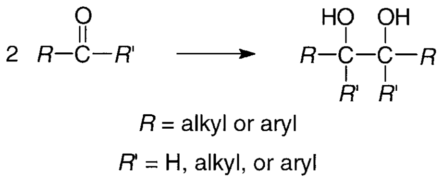


Scheme 1

Table 1. Pinacolization of carbonyl compounds; the entries in the last column refer to isolated yields; physical and spectroscopic (IR, ^{1}H and ^{13}C NMR) data of the products are in agreement with the expected structures; the pinacols are formed as *dl*/*meso* mixtures which have been analyzed only for benzaldehyde (*dl*:*meso* = 40:60) and cinnamaldehyde (*dl*:*meso* = 15:85) as educts

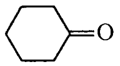
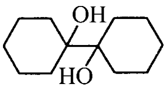
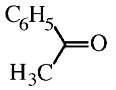
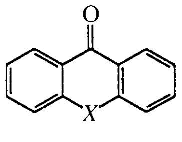
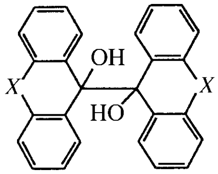
Entry	Carbonyl compound	Pinacol	Yield/%
1	C_6H_5–CHO	$(C_6H_5CHOH)_2$	45
2	C_6H_5–CH=CH–CHO	$(C_6H_5CH{=}CH{-}CHOH)_2$	55
3			45
4	p–Br–C_6H_4–CHO	$(p{-}Br{-}C_6H_4{-}CHOH)_2$	80
5	p–Cl–C_6H_4–CHO	$(p{-}Cl{-}C_6H_4{-}CHOH)_2$	75
6	o–MeO–C_6H_4–CHO	$(o{-}MeO{-}C_6H_4{-}CHOH)_2$	60
7	m–MeO–C_6H_4–CHO	$(m{-}MeO{-}C_6H_4{-}CHOH)_2$	80
8		$(C_6H_5{-}C(CH_3)OH)_2$	40
9	$(C_6H_5)_2C{=}O$	$((C_6H_5)_2{-}COH)_2$	95
			
10	X = *nil*	X = *nil*	85
11	$X = CH_2$	$X = CH_2$	92
12	$X = S$	$X = S$	90
13	$X = O$	$X = O$	95

Table 1, the reaction of substituted benzaldehydes (entries 1, 4–7), cinnamaldehyde, or acetophenone gives *dl*/*meso* mixtures of pinacols. Due to its high yields and its speed, the method is competitive with many other ways of pinacol formation [2–8]. Especially, the yields obtained in the coupling of aromatic aldehydes substituted by Cl, Br, or OCH_3 deserve interest.

In conclusion, the zinc-promoted reductive coupling of aldehydes and ketones in aqueous media turned out to be remarkably effective in pinacolization. This method is a relatively rapid, manipulatively simple, and inexpensive protocol when compared with other methods which are disadvantageous concerning expensive catalysts, long reaction times, and tedious work up.

Experimental

Melting points were measured with an Electrothermal 9100 apparatus and are uncorrected. IR spectra were recorded on a Philips PU 9800 FT-IR instrument. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-90A spectrometer at 90 and 22.6 MHz. All compounds have been reported in the literature; their physical and spectroscopic data were in accordance with those of authentic samples.

General procedure

Zn powder (4 mmol, 0.26 g) and carbonyl compound (2 mmol) were slurried in 3 cm^3 saturated aqueous NH_4Cl and 5 cm^3 *THF*. The mixture was stirred at room temperature. The temperature rose, and after 10 min the Zn powder had disappeared. The solvents were evaporated to dryness, and the product was extracted with diethyl ether. The etheral layer was separated and evaporated to dryness to afford the pure pinacol.

References

[1] Robertson GM (1991) In: Trost BM (ed) Comprehensive Organic Synthesis. Pergamon Press, Oxford, vol. 3, p 563; Kropf H, Thiem J (1973) In: Houben-Weyl, Methoden der Organischen Chemie, vol. 6/1b/2, Thieme, Stuttgart, p 1458
[2] Ito K, Nakanishi S, Otsuji Y (1980) Chem Lett 1141
[3] Hiyama T, Obayashi M, Mori I, Nozaki H (1983) J Org Chem **48**: 912
[4] Inoue H, Suzuki M, Fujimoto N (1979) J Org Chem **44**: 1722; Hou Z, Takamine K, Fujiwara Y, Taniguchi H (1987) Chem Lett 2061
[5] Chen TL, Chan TH, Shaver A (1984) J Organomet Chem 268, C1
[6] Clerici A, Porta O (1983) J Org Chem **48**: 1690; (1983) Tetrahedro **39**: 1239
[7] Corey EJ, Danheiser R, Chandresekaram S (1976) J Org Chem **41**: 260
[8] Furstnur A, Csuk R, Rohrer C, Weidmann H (1988) J Chem Soc Perkin Trans 1, 1729
[9] Lubineau A, Auge J, Queneau Y (1994) Synthesis 741
[10] Imai T, Nishida S (1993) Synthesis 395
[11] Einhorn C, Einhorn J, Luche JL (1989) Synthesis 787

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