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Reductive Coupling Reaction of Carbonyl Compounds Using Al Powder in 10% aq NaOH/MeOH/THF Solution ^{1),2)}

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Reductive coupling reaction of benzaldehydes, acetophenone, ethyl phenyl ketone and 1-tetralone using Al powder in 10% aq NaOH/MeOH/THF solution afforded the corresponding ethane-1,2-diols.

Introduction

The reductive C-C coupling reaction of carbonyl compounds³⁾ is an important method for the preparation of ethane-1,2-diols and Al (Hg)⁴⁾, TiCl₄-Zn⁵⁾, Ce-I₂⁶⁾, SmI₂⁷⁾, Mg-Graphite⁸⁾, Me₃SiCl/NaI/Sm⁹⁾ and Sm (OTf)₂¹⁰⁾ have been widely used. These reagents are moisture-sensitive and have to be handled under dry inert atmosphere with tedious procedures. Only a few metallic reagents such as TiCl₃¹¹⁾, Al (Hg)¹²⁾, and Zn-ZnCl₂¹³⁾ have been reported for the reductive coupling reactions under aqueous conditions. Recently, pinacolization of aromatic carbonyl compounds with Al powder and KOH in MeOH was reported.¹⁴⁾

We previously reported that the treatment of benzaldehyde (1a) with Raney Cu-Al alloy in 10% aq NaOH solution afforded 1,2-diphenyl-1,2-ethanediol (3a) in poor to moderate yields (5-32%), besides benzyl alcohol¹⁵ and that **3a** was selectively obtained in a low yield (30%) by using Al powder under the same conditions with the recovery (50%) of 1a.¹⁵ We now report the treatment of carbonyl compounds using Al powder in an alkaline media to afford 1,2-ethanediol derivatives in good yields.



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Table 1 Solvent Effect on the Reductive Coupling Reaction of (1).^{a)}

solvent ^{b)}	Product (%) ^{c)}		Recovery of 1a	
	2a	3a	la	
MeOH	8(trace ^d)	92 (46 ^{d)})	0	
THF	9	9	82	
THF/MeOH	$7(\text{trace}^{d})$	93(75 ^{d)})	0	
THF/EtOH	1	3	96	
THF/i-PrOH	2	2	96	

a) **la**/Al/10% aq NaOH=50mmol/1.25g/20ml.r.t., 100min. b) MeOH, EtOH, or i-PrOH!THF = 35mmol/10ml. c) Relative yields determined by G.C. d) Isolated yield.



Table 2 The Reductive Coupling Reaction of (1) in an Alkaline Solution.^{a)}

Substrate	Product	Yield (%) ^{b)}	dl/meso ^{c)}
la	3a	75	46/54
1b	3b	81	57/43
1c	3c	75	58/42
1 d	3d	72	50/50
1e	3e	62	60/40
1 f	3f	66	88/12
1 g	3g	91	55/45
1h	3h	86	57/43
1i	3i	80	60/40
1j	3ј	47	67/33

a) r.t., 100min. b) Isolated yield. c) Ratios determined from the intensities of benzylic protons in 1 H-NMR spectra, in which the protons of dl form appeared at a higher magnetic field, compared to the one of meso isomer.^{8).16)-18)}

Results and Discussion

The coupling reaction of **1a** using Al powder in 10% aq NaOH-MeOH alkaline gave **3a** in 46% yield (**Scheme 2** and **Table 1**). Though THF itself is less effective, a mixed solvent of MeOH and THF gave **3a** in 75% yield. It was found that MeOH is essential for the reaction and that EtOH and *iso*-PrOH are ineffective. As alkaline solutions, a 10% aq KOH solution afforded the expected **3a** just as a 10% aq NaOH solution, but a 10% aq LiOH solution gave a little of **3a**. The coupling reaction of **1a** did not proceed in a 10% aq CsOH or a 10% aq Na₂CO₃ solution.

From the results above mentioned, the coupling reactions of **1b**-**j** were carried out using Al powder in a mixed solvent of 10% aq NaOH, MeOH and THF and the corresponding 1,2-ethanediols **3b**-**j** were given in good yields (**Scheme 3** and **Table 2**). The (dl/meso) ratios of **3a**-**j** were determined by ¹H-NMR ^{8),16)-18)} to be almost 1 : 1. Attempted cross coupling reac-



Table 3	Table 5 Coupling Reaction of Retone (5).		
Substrate	Temp.	Isolated yield (%) of 6°	
5a	room temp.	6a (35)	
5a ^{b)}	room temp.	6a (75)	
5 b ^{b)}	45℃	6b (43)	

D ...

C 17 .

m 11

a) 100min. b) Under ultrasonic irradiation. c) dl/meso Ratios were determined by¹ H-NMR^{8),19} as 51/49 for **6a** and 79/21 for **6b**, respectively.



tion of **1a** and **1b** gave the expected **3a**, **3b** and cross-coupled **3k** in a 1:1:1 ratio (Scheme 4).

The reductive coupling reaction of acetophenone (5a) gave 6a in 35% yield. Ultrasonic irradiation increased the yield of 6a to 75%. The reaction of ethyl phenyl ketone (5b) proceeded at a elevated temperature $(45^{\circ}C)$ under sonication to afforded 6b in 43% yield (Scheme 5 and Table 3).

Similarly tetralone (5c) gave dl-1,1'-dihydroxy-octahydro-1,1'-binaphtalin 6c, but in poor 19% yield (Scheme 6).

Aldehydes such as 2-hydroxy-, 4-hydroxy-, 4-phenyl- and 4-benzyl-oxybenzaldehyde, 1and 2-napthaldehyde as well as cyclohexanone and 9-fluorenone are inert towards the treatment with Al powder under the similar conditions.

Finally, Al powder is useful for the reductive coupling reaction of carbonyl compounds in a mixed solvent system of 10% aq NaOH solution, MeOH and THF under mild conditions with easy operations.

Experimental

General. Vapor-phase chromatography was performed on a Yanagimoto Gas Chromatograph G-2800 instrument equiped with a fused-silica capillary column (Quadrex corporation, 007-1-25-0.25F, 0.25 mm i. d. X 25 m, liquid phase: methyl silicone). Product identification was carried out based on the retention time of standard materials (**1a**, **2a**, and **3a**). An ultrasonic clearner (Elma Transsonic T 460, frequency 35 KHz, acoustic power 68 W, capacity 2L) was used for sonication durring coupling reaction. Column chromatography was carried out on silica gel (Wako-gel, C-300).

Materials. Benzaldehydes **1a**-**j** and ketones such as **5a**-**5c** are commercially available. Commercially available Al powder was used for the reaction (mesh 150, Kishida Chemical Co.).

Reductive Coupling Reaction of Benzaldehydes: General Procedure.- To a stirred mixture of benzaldehyde (**1a**) (5.30g, 50mmol), Al powder (1.25g), MeOH (35ml) and THF (10ml) at room temperature was added gradually 10 % aq NaOH solution²⁰⁾ (20ml) for 10 min. After the reaction mixture was stirred for 90 min at room temperature, Al powder was filtered off with filter aid and the filtrate was extracted with dichloromethane. The extracts were washed with water, dried (MgSO₄) and evaporated *in vacuo* to leave a residue. Recrystallization (hexane-ethyl acetate) of the residue gave 1,2-diphenyl-1,2-ethanediol (**3a**) (4.01g, 75%) as a mixture of dl⁻²¹⁾ and meso⁻⁸⁾ isomer (dl/meso=46/54).

Reductive Coupling Reaction of Ketones: General Procedure.- To a stirred mixture of acetophenone (**5a**) (6.00g, 50mmol), Al powder (1.25g), MeOH (35ml) and THF (10ml) at room temperature was added gradually 10% aq NaOH solution (20ml) for 10 min under ultrasonic irradiation.²²⁾ Then the reaction mixture was stirred for 90 min under the same reaction conditions. The work-up, as described above, gave 2,3-diphenyl-2,3-butanediol (**6**) (4.53g, 75%) as a mixture ⁸⁾ of dl and meso form (dl/meso=51/49).

References

- 1) M. Tashiro, S. Mataka, T. Tsukinoki, K. Ishimoto and H. Tsuzuki, presented at the 65th Spring Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1993, Abstract of Papers, II: p193 (1993).
- 2) When the manuscripts were under preparation, the authors notified a similar research work on pinacol formation from benzaldehydes using Al under ultrasonic irradiation by a group of T. Thiemann, L. Sa e Melo, and A. S. Campos Neves, which soon will be submitted in J. Chem. Res.
- 3) G. M. Robertson, "Comprehensive Organic Synthesis," vol 3, pp563-610, B. M. Trost, Pergamon Press, Oxford, 1991.
- 4) A. A. P. Schreibman, Tetrahedron Lett., 4271 (1970).
- 5) T. Mukaiyama, T. Sato and J. Hanna, Chem. Lett., 1041 (1973).
- 6) T. Imamoto, T. Kusumoto, Y. Hatanaka and M.Yokoyama, Tetrahedron Lett., 23, 1353 (1982).
- 7) J. L. Namy, J. Souppe and H. B. Kagan, Tetrahedron Lett., 24, 765 (1983).
- 8) A. Fürstner, R. Csuk, C. Rohrer and H. Weidmann, J. Chem. Soc., Perkin Trans. 1, 1729 (1988).
- 9) N. Akane, Y. Kanagawa, Y. Nishiyama and Y. Ishii, Chem. Lett., 243 (1992).
- 10) T. Hanamoto, Y. Sugimoto, A. Sugino and J. Inanaga, Synlett, 377 (1994).
- 11) A. Clerici and O. Porta, Tetrahedron Lett., 23, 3517 (1982).
- 12) M. Hulce and T. LaVaute, Tetrahedron Lett., 29, 525 (1988).
- 13) K. Tanaka, S. Kishigami and F. Toda, J. Org. Chem., 55, 2981 (1990).
- 14) a) J. M. Khurana and A. Sehgal, J. Chem. Soc., Chem. Commun., 571 (1994). b) J. M. Khurana, A. Sehgal, A. Gogia, A. Manian and G. C. Maikap. J. Chem. Soc., Perkin Trans. 1, 2213 (1996).
- 15) T. Tsukinoki, K. Ishimoto, H. Tsuzuki, S. Mataka and M. Tashiro, Bull. Chem. Soc. Jpn., 66, 3419 (1993).
- 16) J. H. Stocker, D. H. Kern and R. M. Jenerein, J. Org. Chem., 33, 412 (1968).
- 17) M. Imuta and H. Ziffer, J. Org. Chem., 43, 3319 (1978).
- 18) R. E. Balsells and A. R. Frasca, Tetrahedron, 38, 2525 (1982).
- 19) D. Seebach, H-A. Oei and H. Daum, Chem. Ber., 110, 2316 (1977).
- 20) The coupling reaction of **1a** also proceeded by using 1% aq NaOH solution (200 ml)/MeOH/THF, in place of 10% aq NaOH solution (20ml)/MeOH/THF, giving **3a** in a similar yield and in a similar dl/meso ratio. On the other hand, when 20% aq NaOH solution (10ml)/MeOH/THF was used, **3a** was obtained in a similar dl/meso ratio but in a lower yield.
- 21) A. Collet, Synthesis, 664 (1973).