

A Simple and Efficient New Synthesis of Vicinal Diols by Reductive Coupling of Carbonyl Compounds

René Csuk, Alois Fürstner, and Hans Weidmann*

Institute of Organic Chemistry, Technical University Graz, Stremayrgasse 16, A-8010 Graz, Austria

A universally applicable, new 'pinacolic reduction' for aldehydes and ketones is described.

Among the various reductions of carbonyl compounds, those leading to coupling products¹ are of greatest and continuing interest. Since the discovery of the coupling of carbonyl compounds to yield alkenes, *i.e.* the McMurry reaction,² which was shown generally to proceed *via* vicinal diols,³ considerable attention has been directed at improving the accessibility of these intermediates. The most useful and general 'pinacolic reduction,' presently favoured,⁴ uses Mg/Hg to reduce TiCl₄,⁵ thus combining classical⁶ and recent methodology; however, since low-valent Ti-reagents, favoured for such reductions,^{4,5,7,8} pose problems concerning

their oxidation state⁴ and are also liable to form olefinic by-products,⁴ we decided to search for a simpler route to vicinal diols.

After a substantial improvement of the reactivity of metals was obtained by C₈K-reduction of metal salts,⁹ leading to considerable progress in organometallic reactions,^{9,10} Mg-graphite was found to be a simple, universally applicable, and mercury-free reagent for 'pinacolic reductions.' In contrast with Ti-^{7,8} or Ce-based¹¹ reactions and in accord with Corey's method,⁵ Mg-graphite rapidly and invariably reduces a variety of carbonyl compounds to vicinal diols, under various

Table 1. % Yields of vicinal diols by 'pinacolic reduction' of carbonyl compounds using Mg-graphite, compared with those obtained by previously reported methods.^a

	Mg-graphite, ambient temp. ^b	Al/Hg, reflux	Mg/Hg, reflux	Mg/MgI ₂ , reflux	Ce/I ₂ , ambient temp. ^c	TiCl ₄ /Zn, ambient temp.	Mg/Hg/TiCl ₄ , 0 °C
Benzophenone	91 (2 h)	32 (4 h) ^e	0 ^e	99.6 ^h	0 (14 h)	—	—
Acetophenone	78 (4 h) ^d	21—38 (4 h) ^f	Low ^g	—	88 (14 h)	91 (2 h) ⁱ	—
Benzaldehyde	93 (0.7 h) ^d	Low ^f	—	0 ^h	94 (14 h)	98 (2 h) ⁱ	84 ^j
Cyclohexanone	84 (4 h)	55 (4 h) ^f	35 ^h	—	95 (14 h)	24 ^j	93 (0.5 h) ^j
Cyclopentanone	82 (4 h)	31—40 (4 h) ^f	—	—	84 (14 h)	—	95 (0.5 h) ^j
Pentan-3-one	65 (2 h) ^k	—	16.5 ^h	—	—	—	—
Octanal	87 (0.3 h) ^d	—	—	—	—	—	80 (13 h) ^j

^a All compounds gave satisfactory microanalytical and spectral data. Reaction time in parentheses where reported. ^b At reflux no change in yields. ^c Ref. 11. ^d Diastereoisomeric mixture. ^e Ref. 14. ^f Ref. 13. ^g Ref. 15. ^h Ref. 6. ⁱ Ref. 7. ^j Ref. 5. ^k Pentan-3-ol (20%) as by-product.

conditions.† There is only one reference on the reduction of benzophenone to give benzpinacol using active Mg-metal.¹² It is noteworthy that aluminium, known to be a powerful one-electron donor,¹³ when applied in the form of mercury-free Al-graphite, was found to be unsuitable for 'pinacolic reductions.' Thus, the Mg-graphite reduction of carbonyl compounds appears to be of potential use and may provide an economical 'pinacolic coupling' of universal applicability.

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† To a suspension of 0.1 mol C₈K, prepared according to ref. 9, in 30 ml of anhydrous tetrahydrofuran (THF), 0.05 mol of MgCl₂ was added at ambient temperature, heated at reflux for 30 min and cooled. After addition of 0.05 mol each of the carbonyl compound in 4 ml of THF and stirring for the time shown in Table 1 (preferably at ambient temperature), the mixture was filtered, diluted with diethyl ether, and extracted with water. Evaporation and chromatography resulted in pure, crystalline products.