



Reductive Coupling of Benzaldehyde Mediated by Camphor

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ABSTRACT

A very simple alternative procedure for the reductive coupling of benzaldehyde mediated by camphor is developed.

Key words: Reductive coupling, benzaldehyde, camphor, diol.

INTRODUCTION

1, 2 diols are one of the most frequently available organic compounds in nature and as a result of that a wealth of methods have so far been developed for its synthesis. Some important of them are, catalytic osmylation of olefins¹, ring opening epoxides², reduction of 1, 2 diketone or alkylation of α -hydroxy or α -alkoxy carbonyls³, reaction of an alkoxy anion⁴ with carbonyl and the reductive coupling of two carbonyls⁵ and similar methodologies⁶⁻⁸. However, all these methods for the synthesis of 1,2 diols have proven elusive. In most of the cases it needs/several hours to complete and the yields are generally low. The initial stage of all the reductive coupling of the corresponding aldehydes or ketones turn into a gel which is difficult to handle and the subsequent stages associated with darkening and transformation⁹. A number of side products are frequently obtained along with the derived product which makes a purification process a tedious one. The alternative photo induced radical dimerisation process needs prolong exposure of the reaction mixture in the intense light. Due to these reasons such type of reactions are not effective for practical purposes.

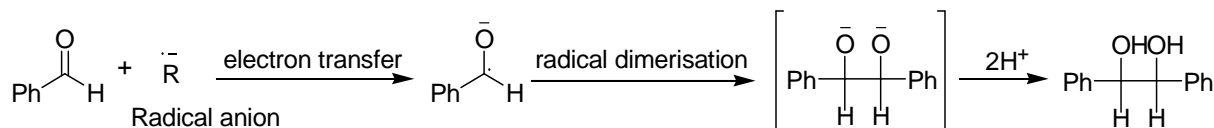
Herein, we describe a very simple alternative procedure for the reductive coupling of benzaldehyde mediated by camphor. It took relatively shorter time to completion and yielded exclusively the desired diol with 70% yield.

EXPERIMENTAL SECTION

Commercial camphor (1 g) was purified by method of sublimation and was dissolved in dry, distilled ether (50ml). Ether washed molecular sodium was introduced in batches into the reaction vessel and the reaction temperature was maintained below 10 °C in an ice bath. No nitrogen was flashed and the reaction mixture was stirred for 15 minutes, the initially formed white precipitate was dissolved to form a transparent liquid. Few drops of ethanol were introduced to neutralize the excess sodium. Distilled benzaldehyde was then added slowly with constant stirring for another 30 minutes. A white precipitate obtained was then filtered, washed with water and extracted with ether. Evaporation of the solvent yielded a white solid (0.5 g) which was recrystallized from dry ether.

RESULTS AND DISCUSSION

A systematic survey of reductive coupling of carbonyl compounds¹⁰ and the probable mechanism involved there¹¹⁻¹² (scheme-I) prompted us to make a preliminary observation of such kind of coupling mediated by camphor, which is prone to mediate the electron transfer. It was anticipated that intermolecular cross coupling might be possible if an aldehyde/ketone was slowly added to a purified solution of camphor in ether prior treated with sodium, if **scheme I** were operative.



Scheme I

As a model we took benzaldehyde in our preliminary work (see experimental). The single product (TLC) with a 70% of yield, obtained after 1 hr of reaction was characterized by spectroscopic methods (IR, NMR and Mass). NMR data of product (I) indicated the formation of a diastereomeric product mixture in 1:1 ratio, which is in close agreement with the earlier observation of such kind of reductive coupling carried out using other reducing agents¹⁰. The structure of the diastereomeric products was also confirmed by the mass spectral data. The mechanism of formation of the product may be explained by assuming the formation of radical anion (scheme-I). It is also reported that radical anions are generally stable species if generated by exposure to alkali metals or by electrolytic reduction of carbonyl compounds. This was preliminary study, however, detailed investigation aimed at further confirmation of the reactive intermediate involved in the reactions as well as to improve the diastereoselectivity of these reactions are underway.

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