

Optically Active Lithium 1,2-Diphenyl-1,2-Ethanediolate: An Efficient Chiral Auxiliary In The Enantioselective Hydrosilylation Of Ketones.

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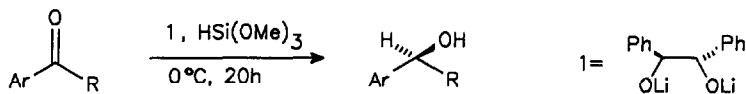
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Abstract. In the asymmetric hydrosilylation of ketones employing lithium (1*S*,2*S*)-1,2-diphenyl-1,2-ethanediolate as chiral ligand of trimethoxysilane, alkylarylcarbinols were obtained with yield up to 95% and e.e. ranging from 12 to 82%.

The reduction of prochiral ketones, by means chirally modified hydrides, constitutes an useful system for the preparation of optically active alcohols¹. Recently this reaction was carried out employing "chiral" silicon hydrides, which are obtained by treating trimethoxysilane with an optically active lithium dialcoholate²: in this way, a pentacoordinate hydrosilane was obtained, which acts at the same time as Lewis acid, activating the carbonyl group of the substrate toward the nucleophilic addition, and as nucleophile, transferring the hydride ion on the activate carbonyl group³. In this communication we report the results obtained in the reduction of alkylarylketones, employing as chiral ligand of trimethoxysilane the lithium dialcoholate of (1*S*,2*S*)-1,2-diphenyl-1,2-ethanediol, **1**, which is easily obtainable⁴ and has not been yet used in this reaction. The results obtained⁵ (yield, e.e., absolute configuration of the prevailing enantiomer) are summarized in the Table. The chemical yields depend on the bulkyness of the carbonyl substituents: as a matter of fact when the aryl fragment is the 1-naphthyl group, which is crowded owing to the presence of the peri hydrogen near to the site of reaction, lower yields of the corresponding alkylarylcarbinol are obtained. The lower yields are attributable³ to the difficult coordination of the carbonyl oxygen to the silicon atom: if this coordination is practically prevented, as in the case of highly crowded 1-naphthyl-*t*-butylketone, the starting material is quantitatively recovered. Very good yields are obtained by reacting phenyl and 2-naphthylalkylketones, except in the case of phenyl-*t*-butylketone; this anomalous behaviour can be explained considering a different reaction mechanism for this substrate. As far as the enantioselectivity is concerned, low chemical yields correspond to low e.e. (12-22%); and it seems reasonable that a weak coordination of the carbonyl oxygen to the silicon is also responsible of the low asymmetric induction from the chiral ligand **1**. In the other cases the e.e. of the product change depending on the nature of the alkyl substituent in the order *t*-Bu < Me < *i*-Pr, the aryl fragment being the same: this behaviour has been already observed in other kinds of enantioselective reductions of alkylaryl ketones⁶. In all the considered cases, the carbinol having the *S* absolute configuration was prevailingly obtained. Therefore, the use of the chiral pentacoordinate hydrosilane obtained from **1** can

constitute a practical and efficient route to obtain alkylarylcarbinols in very good yields and e.e. ranging from 12 to 82%. In addition must be considered that the chiral ligand, although it is used in stoichiometric amount, is recovered easily and almost quantitatively. Finally, the accessibility to optically active 1,2-diols, by means of the *cis*-dihydroxylation of prochiral olefins by the Sharpless method⁴, allows to study the influence of their structure on the course of the reaction.

TABLE. Enantioselective hydrosilylation of alkylarylketones by trimethoxysilane and **1**.



Ar	R	Yield % ¹	e.e. % ²	a.c. ³
Phenyl	Methyl	93	28	S
Phenyl	<i>i</i> -Propyl	95	42	S
Phenyl	<i>t</i> -Butyl	59	12	S
2-Naphthyl	Methyl	93	65	S
2-Naphthyl	<i>i</i> -Propyl	>95	82	S
2-Naphthyl	<i>t</i> -Butyl	>95	20	S
1-Naphthyl	Methyl	59	22	S
1-Naphthyl	<i>i</i> -Propyl	50	20	S
1-Naphthyl	<i>t</i> -Butyl	-	-	-

1. Percentage determined by ¹H NMR analysis; 2. By HPLC analysis using ionic Pirkle DNPBG column (see ref. 7); 3. Absolute configuration assigned from elution order (see ref. 7).

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- In a typical procedure the dilithium salt **1** was prepared from optically active (1*S*,2*S*)-1,2-diphenyl-1,2-ethanediol (1.2 mmol) and *n*-butyllithium (2.4 mmol) in dry THF (10 ml) at 0°C. To this solution, a solution of the ketone (0.5 mmol) and trimethoxysilane (0.6 mmol) in dry THF (10 ml) was slowly added at 0°C and the reaction mixture was stirred at the same temperature for 20 h. Diethyl ether (20 ml) and 10% HCl (10 ml) were added and, after usual work-up, the alkylarylcarbinol was separated, by means column chromatography (SiO₂, CHCl₃) of the crude product, from the chiral ligand, which was recovered in 90% yield and unchanged optical purity.
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