Notes

Reductive Coupling of Carbonyl Compounds using Silole and Germole Dianions

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Summary: Reductive coupling of aryl aldehydes and ketones is induced by silole and germole dianions at −78 °C in THF, and 1,2-diols are obtained as the only or major products.

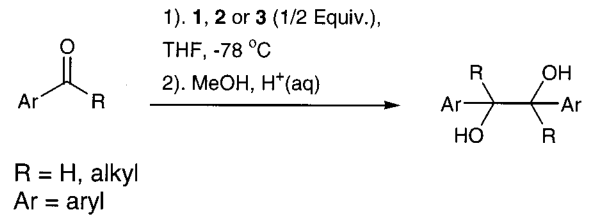
Introduction

Carbonyl coupling reactions, such as McMurry reduction, are of great importance as a synthetic tool in organic synthesis.[1−3] For these types of reactions metals and metal complexes are most often used as reducing agents. Herein we report the first example in which silole and germole dianions (**1**−**3**) are used for the reductive coupling of aryl aldehydes and ketones to give 1,2-diols (Scheme 1). The coupling reactions are carried out at −78 °C in THF, very mild conditions compared with the reactions induced by alkali metals, in which room temperature or higher is usually required. Only a few metal complexes, such as SmI_2, can accomplish the pinacolization reaction at −78 °C.[4] The dianion coupling reactions probably proceed by dimerizations of carbonyl radical anions formed by single electron transfer from the dianion. In most cases, the reaction gives the 1,2-diol as the only product, instead of a mixture of a diol and an alkene. Thus, this coupling reaction may provide a useful alternative method for carbonyl coupling.

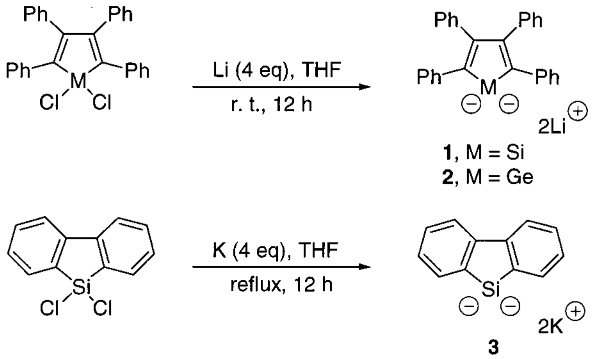
Results and Discussion

The dianions **1**−**3** are prepared by alkali-metal reduction of the corresponding dichlorides (Scheme 2).[5−8]

Scheme 1



Scheme 2



Dianions **1**−**3** can transfer up to two electrons to the carbonyls, and thus the ratio of C═O to dianion is 2:1 in these coupling reactions. During the reaction, the dianions are oxidized to radicals or radical anions which subsequently undergo homopolymerization to give oligosilanes.

Reductive coupling reactions of various aldehydes and ketones induced by dianions **1**−**3** are listed in Table 1. Generally, aldehydes are more reactive and give higher yields than ketones. Aromatic aldehydes with electron-donating ortho substituents gave the highest yields, over 90%, while those having meta and para substituents gave yields of 30−70%. No apparent substituent effect was found in the ketone reactions.

The stereoselectivity of these reactions is generally weak, with only a slight to moderate favoring of *dl* over *meso* products. Reaction of 1-naphthaldehyde, however, is highly diasteroselective, with *dl*:*meso* = 48:1. The

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[5] Substituted (tetraphenyl or fluorenyl) dianions were used rather than unsubstituted metallole dianions because of the instability of the latter. For a review on metalloles, including metallole anions, see: Dubac, J.; Guerin, C.; Meunier, P. In *The Chemistry of Organic Silicon Compounds*; Vol 2; Rappoport, Z., Apeloig, Y., Eds.; Wiley: New York, 1998; Vol. 2, Chapter 34, pp 1961−2036.

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Table 1. Reductive Coupling of Carbonyl Compounds ArCOR with Dianions 1-3.[A,7]

Ar	R	dianion	yield of diol, %[b]	*dl*:*meso*[b]
Ph	H	**1**	93.0	3:1
o-MePh	H	**1**	92.8	1:1
p-MePh	H	**1**	49.5	1:1
m-MePh	H	**1**	63.0	1:1
o-MeOPh	H	**1**	92.8	3:2
p-MeOPh	H	**1**	67.6	2:1
m-MeOPh	H	**1**	51.9	7:5
o-ClPh	H	**1**	93.9	1:1
p-ClPh	H	**1**	51.5	2:1
m-ClPh	H	**1**	33.5	1:1
1-naphthyl	H	**1**	92.5	48:1
2-naphthyl	H	**1**	93.0	3:1
2,4,6-Me_3Ph[c]	H	**1**	31.0	7:1
Ph	Me	**1**	81.1	4:1
o-ClPh	Me	**1**	34.0	2:1
p-ClPh	Me	**1**	54.1	1:1
m-ClPh	Me	**1**	73.0	4:1
o-MeOPh	Me	**1**	78.0	1:1
p-MeOPh	Me	**1**	15.8	3:1
m-MeOPh	Me	**1**	69.2	3:1
1-naphthyl	Me	**1**	18.4	1:1
2-naphthyl	Me	**1**	71.2	3:1
Ph	H	**2**	88.6	5:2
Ph	Me	**2**	92.5	3:1
p-ClPh	Me	**2**	30.7	4:1
o-MeOPh	Me	**2**	26.5	1:1
p-MeOPh	Me	**2**	17.6	3:1
m-MeOPh	Me	**2**	60.0	3:1
2-naphthyl	Me	**2**	47.9	4:1
Ph	H	**3**	96.8	4:1

[a] The structures of the diol products were confirmed by ^{1}H NMR on the basis of the data from the literature.[1,2] [b] Yields and ratios determined from ^{1}H NMR analysis. [c] The major product was 1,2-dimesitylethene in 68.0% yield.

reaction of the corresponding ketone, 1′-acetonaphthone, showed no selectivity, with *dl*:*meso* = 1:1.

Unlike the McMurry reaction, alkene products were not observed in most reactions. An exception was the reaction of mesitylacetophenone, which gave a mixture of 31% diol and 68% alkene. When the reaction of benzaldehyde with dianion **1** was carried out in refluxing THF, 1,2-diphenylethene was isolated as the only coupling product in 87% yield, with trans:cis = 5:2.

Coupling reactions with esters, such as methyl benzoate, and alkyl aldehyde or ketones were unsuccessful. Intramolecular coupling reactions are still under investigation.

Experimental Section

Representative Procedure: Reductive Coupling of Benzaldehyde by Dianion 3. A solution of 1,1-dichloro-1-silafluorene (2.00 g, 7.97 mmol) in THF (100 mL) was stirred with potassium metal (2.00 g, 51.2 mmol) at 65−75 °C for 12 h. The solution changed to a dark red, and the dianion **3** formed in 80−90% yield.[6] The THF solution of **3** was cannulated into a Schlenk flask containing a THF (100 mL) solution of benzaldehyde (1.69 g, 15.9 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 2 h. Excess methanol (100 mL) was added to quench the reaction. The solution was neutralized with dilute aqueous HCl. The volatiles were removed under reduced pressure, and the residue was extracted with toluene (200 mL). The resulting solution was washed with distilled water, dried with $MgSO_4$, and filtered. The structure of the 1,2-diol was confirmed by ^{1}H NMR[9] and X-ray crystallography. The yield of 1,2-diol was 97.6% and the ratio of the two diastereomers *meso* and *dl* was 1:4 on the basis of ^{1}H NMR data. After preparative GPC column (toluene elution) separation, two major products were isolated: 1,2-diphenyl-1,2-ethanediol (1.65 g, 96.8%) and oligo(silafluorene) (0.81 g, 55.9%). Similar procedures were used for the coupling reactions of the other aldehydes and ketones listed in Table 1.

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