the hydroformylation of simple internal alkenes of low reactivity. A relatively high temperature and low pressure were used to enhance the rate of isomerization and to prevent hydroformylation of the internal alkenes. In the hydroformylation of *trans*-2-octene both ligands **2b** and **2c** showed a high activity and selectivity towards the formation of linear nonanal (Table 2). The hydroformylation of 1-octene formed

Table 2. Hydroformylation of *trans*-2- and -4-octene.[a]

Ligand	Substrate	*t* [h]	Conversion [%][b]	l:b[d]	1-Nonanal [%][c]	TOF[d]
PPh_3	2-octene	1.0	8.5	0.9	46	39
2b	2-octene	1.0	10	9.5	90	65
2c	2-octene	1.0	22	9.2	90	112
PPh_3	4-octene	17	9.0	0.3	23	2.4
2b	4-octene	17	54	6.1	86	15
2c	4-octene	17	67	4.4	81	20

[a] As Table 1, but at 120 °C and with an initial pressure of CO/H_2 (1/1) of 2 bar. [b] Determined by GC with decane as an internal standard. [c] Percentage of linear nonanal in all products other than octenes. [d] See Table 1.

in situ by isomerization was highly favored over the hydroformylation of the large excess of 2-octene, and no hydrogenation was observed. The high selectivity of ligands **2b** and **2c** was even more pronounced in the hydroformylation of *trans*-4-octene; selectivities in the formation of linear nonanal still exceeded 80 % although three consecutive double bond isomerizations had to precede hydroformylation. From these remarkable results it can be concluded that diphosphane rhodium complexes can be very efficient for the selective linear hydroformylation of internal alkenes, an area that seemed hardly accessible. The high activity and selectivity of diphosphanes **2b** and **2c** may open up a new range of applications for hydroformylation catalyzed by diphosphane rhodium complexes. One of the possible interesting industrial applications could be the linear hydroformylation of "Raffinate 2", a mixture of butenes that originates from steam crackers.[1d]

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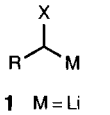
α-Chloroalkylmagnesium Reagents of $>90\,\%$ *ee* by Sulfoxide/Magnesium Exchange**

Reinhard W. Hoffmann* and Peter G. Nell

α-Heterosubstituted organometallic reagents such as **1** are attractive chiral d^1-synthons[1] provided that they have sufficient configurational stability and that they can be generated in high stereochemical purity (Scheme 1). The (α-alkoxy)-



1 M = Li
2 M = MgX

a: X = OR **e**: X = SR
b: X = $OCONR_2$ **f**: X = SiR_3
c: X = NR_2 **g**: X = Cl
d: X = NRBoc **h**: X = I

Scheme 1. The organolithium compounds **1a – h** and the Grignard reagents **2a – h**. Boc = *tert*-butoxycarbonyl.

alkyllithium reagents **1a**,**b**[2] and (α-amino)alkyllithium reagents **1c, d**[3] are prominent examples. Reagents **1**, in which X is a heteroatom of the second row of the periodic table (see **1e**,**f**) have much lower barriers to racemization.[4] Their diminished configurational stability limits their use in stereoselective synthesis. Higher configurational stability may be expected for the corresponding magnesium reagents **2**, since previous studies[5, 6] indicated compounds of the type **2h** to be configurationally stable on a macroscopic time scale at or above $-78\,^\circ C$. We have therefore explored diastereoselective and enantioselective routes to reagents of the type **2**. We

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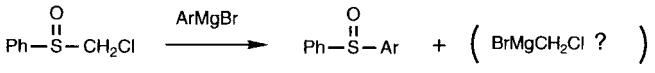
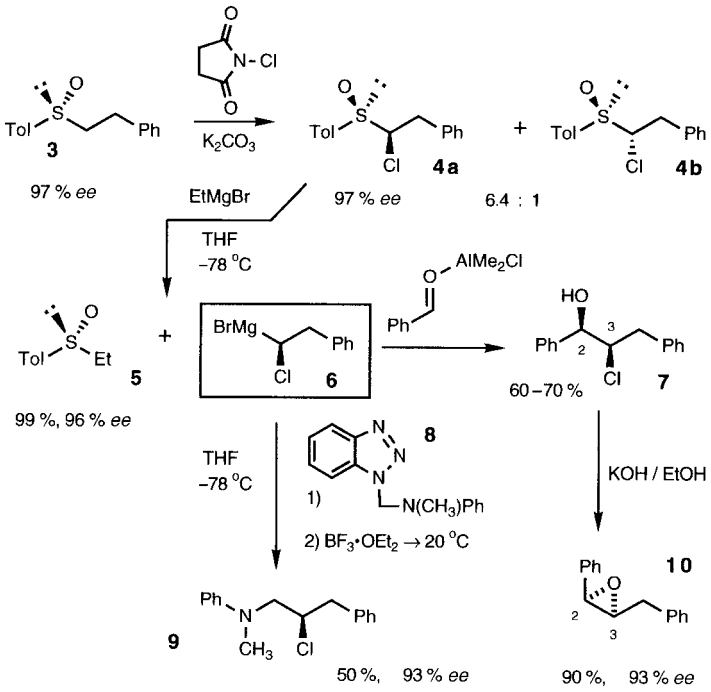
report here on a facile generation of the α-chloroalkylmagnesium reagents **2g** with an enantiomeric excess of larger than 90%.

Our approach is based on the sulfoxide/magnesium exchange reaction,[7] a reaction that has mainly been applied to modify sulfoxides or to generate vinylic[8–10] or cyclopropylic[11, 12] Grignard reagents. But exchange reactions were also reported for α-chloroalkyl sulfoxides (Scheme 2).[13] We



Scheme 2. Exchange reactions with α-chloroalkyl sulfoxides.

adapted this reaction to furnish enantiomerically enriched α-chloroalkylmagnesium compounds **6**: starting point is the (*R*)-(2-phenylethyl)tolyl sulfoxide (**3**) of 99% *ee* ($[\alpha]_D^{20} = +125$ (c = 2.24, acetone); Scheme 3). Chlorination of **3**[11] with *N*-chlorosuccinimide/K_2CO_3 furnished a 6.4:1 mixture of the

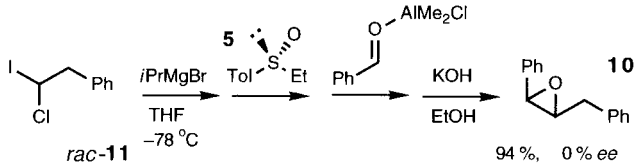


Scheme 3. Synthesis of and reactions with the Grignard reagent **6**.

diastereomeric α-chlorosulfoxides **4**, which could be separated by simple crystallization from acetone. The enantiomeric purity of **4a** (m.p. = 77–78 °C, $[\alpha]_D^{20} = -92$ ($c = 2.00$, acetone) was 97% according to chiral HPLC. The relative configuration of **4b** (and by inference of **4a**) has been secured by X-ray crystal structure analysis. Reaction of **4a** with 1.3 equivalents of ethylmagnesium bromide in THF at −78 °C generated the sulfoxide **5** (99%, $[\alpha]_D^{22} = +198$ ($c = 1.00$, acetone); $[\alpha]_D^{25} = +202.6$[11]) with > 96% *ee* (HPLC) with inversion of configuration at sulfur.[8] Our interest was focused on the Grignard reagent **6** which is generated as a coproduct in this reaction. The Grignard reagent **6** can be trapped at −78 °C by benzaldehyde activated by dimethylaluminum chloride to furnish the chlorohydrin **7** (60–70% yield) in a *syn*/*anti* ratio of 90:10 (only the major diastereomer is shown). The crude chlorohydrins were cyclized to the epoxides **10**, which were obtained in a 88:12 ratio (only the major diastereomer of **10** is shown). ^{1}H NMR spectroscopic analyses in the presence of [Eu(hfc)$_3$] (hfc = 3-(heptafluoropropylhydroxymethylene)-D-camphorate) revealed an enantiomeric purity of **10** of 93% *ee* and showed, with reference to material of known absolute configuration[6, 14] that the major enantiomer of **10** has the configuration (2*R*, 3*S*). The chlorohydrin **7** should therefore have the indicated configuration (2*R*, 3*R*).

The reaction sequence has also been carried out with the *p*-chlorophenyl analogue of **4a** (*p*-ClC_6H_4 instead of *p*-Tol) to provide the chlorohydrin **7** and the epoxide **10** with similar yields and enantiomeric purities. The α-chloroalkyl-Grignard reagent **6** generated in this fashion has been trapped with the α-aminomethylbenzotriazole **8**.[15] The product **9** obtained in 50% yield showed on HPLC analysis with a chiral stationary phase an *ee* value of 93%. The absolute configuration of **9** is assigned in analogy to that of the chlorohydrin **7**.

We postulated that the enantiomeric composition of **6** is derived directly from the diastereomeric purity of the sulfoxide **4a**. To establish that the enantiomeric purity of **6** is not induced in any way by the presence of the chiral coproduct **5**, racemic **6** was generated by reaction of the racemic chloroiodoalkane **11** with isopropylmagnesium bromide at −78 °C. Enantiomerically pure sulfoxide **5**[11] was added after 10 min, followed again after 10 min by benzaldehyde/dimethylaluminum chloride. This reaction resulted in the formation of 94% of the chlorohydrin **7**, which was found to be racemic after conversion to the epoxide **10** (Scheme 4).



Scheme 4. Formation of and reaction with *rac*-**6**.

This study shows that the sulfoxide/magnesium exchange reaction can be applied to generate chiral Grignard reagents **6**. The reaction occurs with retention of configuration at the chlorine-bearing carbon center. Preliminary experiments indicate that the Grignard reagent **6** is subject to a slow racemization under the reaction conditions. Experiments are in progress to delineate to which extent this is a purely thermal racemization or a halide-induced racemization process.[10,16]

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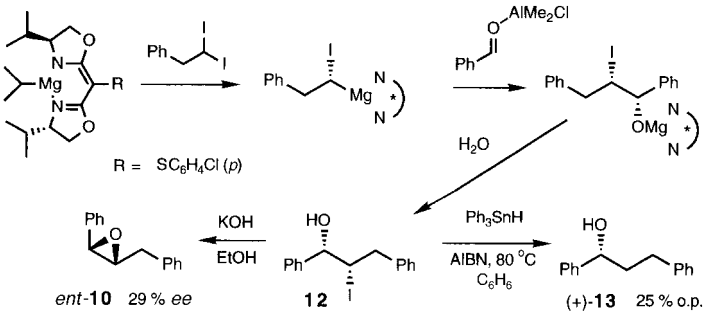

Scheme 5. AIBN = 2,2′-azobisisobutyronitrile; o.p. = optical purity.

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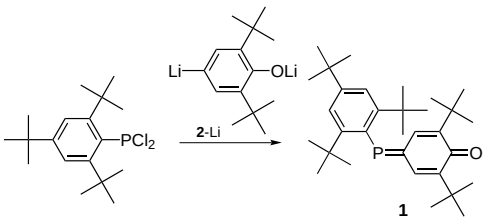
Synthesis, Structure, and Radical Anion of the First Stable *p*-Phosphaquinone**

Shigeru Sasaki, Fumiki Murakami, and Masaaki Yoshifuji*

Dedicated to Professor Edgar Niecke on the occasion of his 60th birthday

Quinoid compounds have attracted considerable interest for a long time owing to their unique structure, properties, and large potential for application.[1] Thus, a variety of quinoid compounds such as quinones, quinodimethanes, and quinodiimines has played an important role in a wide range of research areas. On the other hand, stable quinoid compounds which contain heavier main group elements had not been known until recently, in spite of progress in the chemistry of heavier main group elements, where double bonds between the most of the typical elements and carbon become available. There have been several reports of matrix isolation[2] of the reactive quinoid molecules and isomeric structures such as tetrathiotetracene,[3] but *p*-diphosphaquinone, characterized and reported by Märkl et al.,[4] is the only example of a stable quinoid molecule containing heavier main group elements. However, it has not been obtained in pure form, since not only the quinoid structure but also the double bond between carbon and a heavier element make the species inherently unstable. Here we report the synthesis, structure, redox properties, and generation of the radical anion of the first stable *p*-phosphaquinone **1**. Employment of the 3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dien-1-ylidene moiety, which has been one of the most frequently utilized structures in the chemistry of the quinoid molecules, was essential for the synthesis as well as the effective kinetic protection of **1**.

To construct the quinoid skeleton of **1**, we used the 2,6-di-*tert*-butyl-4-lithiophenoxide ion **2** as a key synthetic intermediate [Eg. (1)], since we expected the extremely high



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