surface of the electrode as one approaches the overpotential for the reduction of D_2O. This hypothesis is born out by the following observations. The competition favoring reaction of $[Rh(diphos)_2]^0$ with D_2O vs. CH_3CN is more pronounced on a Pt electrode than a Hg electrode. The lower overpotential of water on Pt vs. Hg is well established.[12] The age of the HMDE in "wet" acetonitrile solutions greatly influences the reversibility, i_p^{red}/i_p^{ox}, of the Rh^+/Rh^0 couple.[13]

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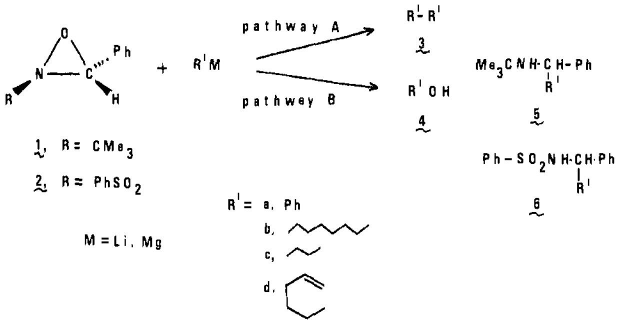
Coupling and Hydroxylation of Lithium and Grignard Reagents by Oxaziridines

Sir:

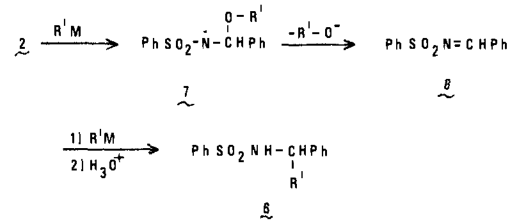
Oxaziridines represent a unique class of three-membered heterocyclic compounds which undergo novel thermal and photochemical transformations.[1,2] At present, the chemistry of these compounds is not well understood. Despite the fact that oxaziridines have been known for nearly 25 years,[3] there appears to have been no study of the reactions of this class of compounds with organometallic reagents. By contrast, the reactions of oxiranes, aziridines, and thiiranes with these reagents have been extensively explored and constitute synthetically useful transformations. Oxiranes give ring-opened products resulting from attack of the lithium and Grignard reagent at the carbon atom adjacent to the oxygen.[4] The situation for aziridines is somewhat more complicated, but similar ring-opened products have been described.[5] Thiiranes, on the other hand, are attacked at sulfur by organolithium compounds to afford the thiol and alkene stereospecifically.[6,7] Grignard reagents react with thiiranes in a manner similar to Grignard reagents with oxiranes and aziridines.[8]

In this context we report that lithium and Grignard reagents (R′M) react in an unprecedented manner with oxaziridines to afford coupling (pathway A) and hydroxylation (pathway B) products (Scheme I). Thus, addition of (*E*)-2-*tert*-butyl-3-phenyloxaziridine (**1**)[9] to a threefold excess of phenyl or *n*-octylmagnesium bromide[10] in ether at 0 °C, afforded after 15 h biphenyl and hexadecane as the principal organic products following hydrolysis with 5% hydrochloric acid (Table I, entries 1 and 2).[11] With *n*-butyllithium **1** gave *n*-octane and adduct **5c** (Table I, entry 4), but with phenyllithium **1** gave phenol and **5a** in good yield (Table I, entry 3).[12]

Scheme I



Scheme II

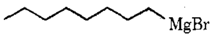
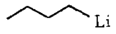
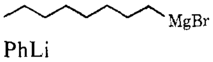
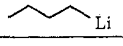


In contrast to oxaziridine **1**, (*E*)-2-benzenesulfonyl-3-phenyloxaziridine (**2**)[1,13] reacts almost exclusively by pathway B with lithium and Grignard reagents (R′M) to afford phenol and alcohols (Table I, entries 5–8). Products were identified by comparison with authentic samples of the reaction products and were isolated by preparative TLC (silica gel).

A mechanism which explains the hydroxylation of R′M by oxaziridine **2** is outlined in Scheme II. In Scheme II we propose that the organometallic reagent (R′M) attacks the oxaziridine oxygen atom to afford intermediate or transition state **7** which collapses to *N*-benzylidenebenzenesulfonamide (**8**) and the hydroxylated product. A similar attack by sulfur on the oxaziridine oxygen atom has been proposed for the selective oxidation of sulfides and disulfides to sulfoxides and thiolsulfinates by **2**.[14] Under the reaction conditions good yields of **6** were obtained when **8** was treated with R′M.

The hydroxylation of organolithium compounds by nitrobenzene[15] and dialkyl peroxides[16] and Grignard reagents by molecular oxygen[17] and *tert*-butyl hydrogen peroxide[18] is reported to occur with varying degrees of success. Hydroxylation of Grignard reagents by oxygen reportedly involves a radical-chain mechanism,[19] while an S_N2 mechanism has been proposed for the formation of ethers from lithium reagents and

Table I. Products of the Reaction of Lithium and Grignard Reagents with Oxaziridines

entry	oxaziridine	temp, °C[a]	organometallic reagent (R′M)	products (% yield)[b] R′OH[c]	R′R′[c]	adduct[d]
1	**1**	0	PhMgBr		**3a** (92–97)	
2	**1**	0	 MgBr		**3b** (85–90)	ref 11
3	**1**	−78	PhLi	**4a** (70–75)		**5a** (95)
4	**1**	−78	 Li		**3c** (82–87)	**5c** (73) + *e*
5	**2**	0	PhMgBr	**4a** (50–58)		**6a** (87–90)[f]
6	**2**	0	 MgBr	**4b** (88–92)		**6b** (63–67)
7	**2**	−78	PhLi	**4a** (92–96)		**6a** (72)[f]
8	**2**	−78	 Li	**4c** (51–61)	**3c** (15)	**6b** (65)

[a] Temperature at which the oxaziridine was added to the organometallic reagent. [b] Products were analyzed by gas chromatography on a 6-ft 6% OV-17 on 60/80 mesh Chromosorb W (regular) column or on a 12-ft 20% Carbowax 20M on 45/60 Chromosorb W (regular) column by comparison of peak areas with standard solutions of the reaction products. Analyses were performed at least twice. Yields are corrected for blank solutions of these compounds in the organometallic reagents. [c] Yields were based on the original concentration of the oxazirdine. [d] Isolated yields. [e] A 15% yield of *N*-*tert*-butylbenzamide was also isolated. [f] H. Stetter and D. Theisen, *Chem. Ber.*, **102**, 1641 (1969).

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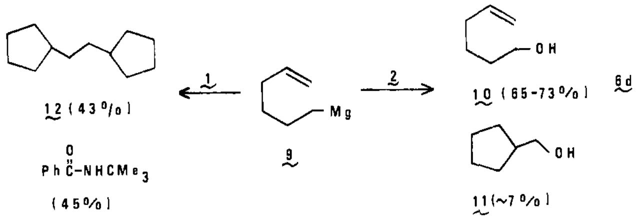

dimethyl peroxide.[20] Miller has argued that the reaction of Grignard and lithium reagents with *o*-quinol acetates to afford ethers occurs by an initial electron transfer (ET) between the organometallic reagent and the *o*-quinol acetate followed by combination of phenoxy and alkyl radicals.[21]

To ascertain whether or not ET mechanisms could account for the hydroxylation and coupling of R′M by oxaziridines (Scheme I) we explored the reactions of **1** and **2** with 5-hexenylmagnesium bromide (**9**).[19,22] Compound **9**, has proven useful for detecting radical intermediates because of the extremely rapid cyclization ($K_{\text{cycl}} = 10^5$ s) of the 5-hexenyl radical to the cyclopentyl methyl radical.[21] Addition of **2** to a 3-fold excess of **9** in ether affords on workup (vide supra) a 65–73% yield of 1-hexen-6-ol (**10**) and ~7% cyclopentylmethanol (**11**).[23] The adduct **6d** was isolated by preparative TLC (silica gel) in 54% yield.[12] The isolation of alcohol **10** in good yield is consistent with the mechanism outlined in Scheme II. If ET had been important, **11** would have been formed in much higher yield.[19] The low yield of **11** undoubtedly occurs by reaction of cyclopentylmethylmagnesium bromide, formed in the preparation of **9**, with the oxaziridine. Similar observations have been reported by others.[22,24]

In contrast to **2**, oxaziridine **1** reacts with **9** to afford a 43% yield of 1,2-dicyclopentylethane (**12**)[25] and a 45% yield of *N-tert*-butylbenzamide.[24,26] ET from R′M to the oxaziridine followed by combination of radical or radical-like intermediates is consistent with these results. The fact that **1** and *n*-octylmagnesium bromide (Table I, entry 2) gave a high yield of hexadecane without any detectable amounts of 1-octene, the disproportionation product, suggests that the coupling reaction (pathway A) involves caged rather than "free" radical species. Coupling of organometallic reagents by various transition metals is well known.[27] These reactions are generally not considered to involve "free" radicals but are believed to be of a bimolecular nature.

The difference in reactivity exemplified by oxaziridines **1** and **2** with organometallic reagents can best be ascribed to the presence of the powerful electron-attracting sulfonyl group which increases the electrophilicity of the oxaziridine oxygen atom and may inhibit ET from R′M to the oxaziridine. Although lithium reagents are reportedly better at transferring an electron than Grignard reagents,[28] the former compounds are much harder nucleophiles than the latter reagents. Perhaps the simplest explanation for the hydroxylation of phenyllithium by **1** and not by *n*-butyllithium (Table I, entries 3 and 4) can be ascribed to the differences in stability between phenyl and *n*-butyl radicals.[29]

Studies aimed at exploring the scope of the reaction of organometallic reagents with oxaziridines are currently in progress.

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Transition Metal Activation of Aldehydes: Platinum Metal Derivatives of *o*-Diphenylphosphinobenzaldehyde

Sir:

The reactivity of aldehydes toward metal ions remains an obscure area of coordination chemistry despite the widespread dependence of the preparations and reactions of the formyl group on metal ion catalysis in industrial synthesis where aldehydes are prepared via palladium catalyzed oxidation and the cobalt and rhodium catalyzed hydroformylation of olefins.[1] Hydrogenations,[2] hydrosilylations,[3] and decarbonylations[4] of the formyl group proceed via platinum metals catalysis; additionally, the hydroacylation of olefins is promoted by rhodium[5] and ruthenium[7] compounds. The prevailing interest in the transition metal induced scission and formation of C–H and C–C bonds[8] renders our synthetic and mechanistic results on these processes especially timely. We find that *o*-diphenylphosphinobenzaldehyde[9] (**1**, abbreviated PCHO) stabilizes intermediates in the reactions of the aldehyde group with

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