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Oxo-Rhenium Catalyzed Reductive Coupling and Deoxygenation of Alcohols

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Abstract. Representative benzylic, allylic and α -keto alcohols are deoxygenated to alkanes and/or reductively coupled to alkane dimers by reaction with PPh₃ catalyzed by (PPh₃)₂ReIO₂ (1). The newly discovered catalytic reductive coupling reaction is a rare C-C bond- forming transformation of alcohols.

The search for efficient processes to convert abundant renewable resources to chemicals and fuels has spurred efforts to develop selective chemical transformations of biomass-derived, oxygen-rich feedstocks by refunctionalizing C-O bonds.¹ Besides dehydration and oxidation,^{2,3} reductive processes that give products with reduced oxygen (and increased energy) content and/or different functionality are receiving attention. Hydrodeoxygenation (HDO, Scheme 1) is one such reaction that is practiced in chemical industry and in the laboratory.⁴ The HDO of activated mono-alcohols (benzylic/allylic/tertiary) can be effected by $H_2/Pd-C^5$ or reaction with Lewis acid/hydridic reagents, proceeding via carbocations.6 Heterogeneous metal- and metal-oxide catalysts, e.g. Pd-C, Ra-Ni and MoS_xO_y, WO_x, ReO_x are used industrially for the HDO of unactivated alcohols and phenols,⁷ but require severe conditions and often have limited product selectivity.8 The homogeneously catalyzed HDO of alcohols is rather little known, but terminal glycols have been converted to terminal alcohols with modest selectivity by low valent Ru-complexes.9 Recently, the selective HDO of aryl ethers¹⁰ and phenols,¹¹ having strong C_{sp2}-O bonds, has been disclosed, catalyzed by nickel and iridium complexes.

An alternative reductive process, deoxydehydration (DODH), involving vicinal-hydroxyl group elimination to give unsaturated products, has been developed recently,¹² catalyzed primarily by oxo-rhenium compounds (Scheme 1) and an expanding set of reductants including PPh₃,¹³ H₂,¹⁴ secondary and activated alcohols,¹⁵ sulfite,¹⁶ elements¹⁷ and hydroaromatics.¹⁸ A catalytic cycle involving a reduced

metalloglycolate that undergoes olefin extrusion appears to be a common feature.^{13-16,19,20} We reported the first DODH reactions catalyzed by non-precious oxo-vanadium complexes,²¹ while others have recently disclosed oxomolybdenum catalyzed DODH with alcohol reductants.²²



Scheme 1. Hydrodeoxygenation (HDO) and deoxydehydration (DODH) of alcohols

The affinity for and activation of alcohols by oxo-metal species illustrated in catalytic dehydration,²³ deoxydehydration,¹² and oxidation²⁴ led us to consider their potential as catalysts for the deoxygenation of mono-alcohols. In this report we disclose a reductant/catalyst system that effects not only the deoxygenation of activated mono-alcohols but also a novel reductive coupling process.

In our initial experiments we sought to demonstrate that an oxo-Re(v) species could stoichiometrically deoxygenate a reactive benzylic alcohol. When benzhydrol, Ph₂CHOH, was heated with (PPh₃)₂ReIO₂ (1)²⁵ (1:1, 150 °C, 24 h, benzene), the major organic product, however, was not the anticipated deoxygenation product, Ph₂CH₂, but rather the dimeric hydrocarbon, *Ph*₂*CHCHPh*₂ (Scheme 2a), formed in over 90% yield along with 5% of (Ph₂CH)₂O.



Scheme 2. Deoxygenation (DO) and reductive coupling (RC) of alcohols

With 1 mol% 1 and PPh₃, benzhydrol was converted to the dimer nearly quantitatively after 7 days (turnover number

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>90, entry 2). The reactions of a number of other alcohols were conducted under the same conditions and the results are summarized in Table 1. Fluorenol was similarly converted to the bifluorenyl (entry 3) in excellent yield, while a cross coupling reaction with benzhydrol/floreneol gave the expected mixture of homo- and heterocoupled products (entry 4). The monoaryl carbinol PhCHMeOH reacted sluggishly forming the corresponding dimer (entry 5). The unsymmetrical allylic substrate, cinnamyl alcohol (entry 6), reacted with PPh₃/1 to give a mixture of regioisomeric diphenyl-1,5-hexadienes in good yield, along with some cinnamaldehyde. The isomeric alcohol, PhCH(OH)CH=CH₂ (entry 7) was converted to a similar isomeric mixture. Sorbyl alcohol was efficiently converted to an isomeric mixture of dimeric tetraenes (entry 8). In contrast, the reaction with Ph₃COH took a different course, producing the deoxygenation product Ph₃CH in good yield (entry 9). Likewise, an αhydroxyketone (entry 10) was efficiently converted to the deoxygenated ketone, rather that the dimer. Benzyl alcohol itself (entry 11) reacted slowly (95h) giving a mixture of benzaldehyde, toluene, the reductive coupling products, PhCH₂CH₂Ph and PhCH=CHPh, and the ether (PhCH₂)₂O. Surprisingly, the mechanistically diagnostic benzylic alcohol 3 was largely unreacted when heated with PPh₃-1 (150 °C. 168h), as were the primary, unactivated alcohol 4 and phenol 5 having stronger C-O bonds (100h).



The catalytic deoxygenation (DO) and, particularly, the reductive coupling (RC) of alcohols reported here find little precedent in homogeneous transition metal catalysis. More established is the deoxygenation of activated alcohols, stoichiometrically by Cp₂TiCl²⁶ and WⁱⁱCl₂(PMe₃)₄²⁷, and catalytically by PMHS/PdCl₂.²⁸ The stoichiometric RC of activated alcohols by reduced Ti-compounds²⁹ and La/Me₃SiCl,^{30a} and a Cu-catalyzed La/Me₃SiCl variant have been reported.^{30b}

A possible catalytic cycle for the deoxygenation and reductive coupling reactions is suggested in Scheme 3, beginning with association of the alcohol with 1 to give an alkoxo-hydroxo species A. Species of this type have been implicated in other oxo-metal-promoted alcohol reactions, e.g. dehydration, oxidation and allylic alcohol isomerization,³¹ Complex A could produce R-H and/or R-R via concerted or stepwise oxidative elimination[§] and generate the oxidized Re(vii) species, (PPh₃)₂ReIO₃ (C); reduction of C by phosphine would regenerate 1. Alternatively, condensation of A with another alcohol molecule would give an oxo-dialkoxo species B, some of which have been characterized.³² Species B also could then undergo oxidative elimination to produce the hydrocarbon dimer. Related reduced metal-alkoxide or -glycolate species have been indicated in the catalytic HDO of alcohols and phenols by reducible solid metal oxides^{8,32} and the homogeneous oxo-

Table 1. Deoxygenation	and	reductive	coupling	of	alcohols
by PPh ₃ /(PPh ₃) ₂ ReIO ₂ (1)	а				

Entry	Substrate	Products	Yield ^b
1	ОН	Ph Ph	80
2 ^d	Ph Ph	Ph Ph	(65) ^c 90
3	OH		91
4	OH Ph Ph + 9-fluorenol (1:1)	$\begin{array}{c} R^{1} & R^{2} \\ R^{1} & R^{2} \\ R^{1} = R^{2} = Ph (24) + \\ R^{1} = R^{2} = 9 - fluorenyl (48) + \\ R^{1} = Ph, R^{2} = 9 - fluorenyl (13) \end{array}$	85
5	OH Ph	$Ph \xrightarrow{Ph} Ph + Ph + Ph (56)$ $(1:1 \text{ meso}: d,l) (56)$	43
6	Ph	Ph 2a (28) Ph Ph Ph Ph	>95 ^e
		Ph = 2b(18) = 2c(18) $Ph = 2c(18)$ $Ph = Ph$ $H = (36)$	
7	Ph OH	2a (30) 2b (17) 2c (17)	>90
8	ОН	C ₁₂ -tetraenes (isomers, 80) + (20)	77
9	OH Ph + Ph Ph	Ph Ph Ph	75
10	Ph Ph OH	Ph Ph	92
11 ^f	Ph OH	Ph - CH ₃ Ph-CHO (PhCH ₂) ₂ O (29) (23) (8) Ph - Ph - Ph	98 ^e
		(13) (25)	

[a] 0.1 M reactants, 0.011 M 1, benzene solvent, 150 °C (sealed tube), 24h; [b]
yields determined by ¹ H NMR integration with Me ₂ NCHO or CH ₂ ClCH ₂ Cl internal
standard; [c] isolated yield after chromatography; [d] 1 mol% 1, 168h; [e] %
conversion of ROH based on NMR; [f] 92h reaction time

metal catalyzed deoxydehydration of $glycols^{13-16,18}$ and epoxide deoxygenation. ^{14,33}

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Scheme 3. Possible catalytic cycle for deoxygenation and reductive coupling

Of key interest is the nature of the C-O bond cleaving step. Some of the known stoichiometric DO and RC reactions have been suggested to occur via the generation of organic radicals from a reduced metal-alkoxide species.³⁴ The substrate reactivity profile (requiring 1-2 aryl or vinyl groups), the reduced and reductively coupled products observed, the limited regioselectivity from the allylic alcohols, and the deoxygenation selectivity for entries 9,10 could potentially be explained by the intervention of carbonradicals derived from either Re-alkoxo intermediate A or B. However, experiments to address this question have thus far failed to definitively implicate C-radical intermediates. Thus, when the benzhydrol-PPh₃-1 reaction was carried out in the presence of 1-2 equiv of the reactive H-atom donors 1,4cyclohexadiene, 9,10-dihydroanthracene or xanthene,³⁵ there was no significant change in the dimer yield (80+5%), nor did products derived from the H-donors appear (Scheme 4). § . §§



Scheme 4. (Non)Effect of H-Donors on reductive coupling

In an initial DFT computational study of the deoxygenation of PhCH₂OH by the model catalyst MeRe^{vii}O₃ $(C')^{II}$ we find the pathway shown in Scheme 3 for 1 to be exoergic at each stage from MeRe^vO₂ (**D**) via intermediates E, A' and C' (Figure 1).[^] A substantially weakened C-O bond in an alkoxy-ReO_x species is indicated by a calculated dissociation energy of only 13 kcal/mol for conversion of $PhCH_2-ORe(O)Me(OH)$ (A') to benzyl radical and F, which increases to 35 kcal for the more accurate model intermediate for catalyst 1, PhCH₂-ORe(O)Me(OH)(PMe₃) (A'->F'), still far lower than for PhCH₂-OH homolysis (81 kcal). While either homolytic or non-homolytic pathways for C-O cleavage in the DO and RC reactions may be operative, a weakened C-O bond in an intermediate Re-alkoxide is likely the source of catalytic activation. The basis for the dimerization/deoxygenation selectivity is an open question that is the focus of on-going mechanistic studies.



Figure 1. Calculated energetics of MeReO₂-promoted alcohol deoxygenation

These novel and direct transformations of alcohols proceed under essentially neutral conditions and avoid the usual additional step of refunctionalizing the alcohol before conversion.³⁸ The direct reductive coupling of alcohols disclosed herein has considerable potential application for upgrading renewable alcohols, providing an alternative to the base-promoted, low selectivity Guerbet reaction.³⁹ Efforts are underway to expand the substrate scope of these reactions, to identify the reactive intermediates and the catalytic pathway involved, and to find more practical and economical reductant/catalyst pairs. In this latter regard we were encouraged to find that the reductive coupling of benzhydrol to tetraphenylethane is also efficiently catalyzed (>75% yield) the reductant/catalyst pair, CO/Bu₄N[(salicyl-2hv thiophenyl-hydrazide) VO_2^{40} (6) [(10 atm CO, 10 mol% 6, 180 °C, 24 h] (Scheme 5).





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Notes and references

^{*} A 1:1 ROH/PPh₃ ratio was used throughout. PPh₃ was almost entirely consumed for the ROH to R-H reactions, but ca. 50% remained for the ROH to R-R reactions, suggesting the stoichiometries: ROH + PPh₃ \rightarrow R-H + OPR₃; 2ROH + PPh₃ \rightarrow R-R + OPR₃ + H₂O.

⁹ The ability of oxo-metal species to catalyze the isomerization of allylic alcohols (ref. 31d-f) also could account for the similar regioselectivity by pre-isomerization of the alcohol substrates.

 99 The selective deoxygenation for entry 9 could result from reversible trityl radical dimerization (ref. 36) and irreversible H-abstraction by Ph₃C from a Re-OH species, e.g. **A**. For entry 10,

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ReO-R homolysis/electron transfer (ref. 37) could generate the stable enolate ion, which abstracts a proton from a Re-OH species.

^{**} MeReO₃ also promotes $Ph_2CH-CHPh_2$ formation from Ph_2CHOH/PPh_3 (1:1:1, 150 °C, benzene), but dehydration to $(Ph_2CH)_2O$ is the major process (1:5.4).

^ The B3LYP method and LANL2DZ/6-31G(d) basis sets were used.

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