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HYDROZIRCONATION. IV.[1] OXIDATION OF ALKYLZIRCONIUM(IV) COMPLEXES TO ALCOHOLS

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Hydrozirconation has been shown to be a convenient route to transform olefins, *via* organozirconium(IV) intermediates, into a variety of desirable organic products.[2,3] We now report that these species $(\eta^5-C_5H_5)_2Zr(R)Cl$ (R = alkyl) can be oxidized under several different, mild conditions to form alcohols in high yield. Since internal olefins are rapidly converted to terminal alkyls by hydrozirconation (except where cyclic olefins are the starting materials), this sequence leads specifically to terminal alcohols from either terminal or internal olefinic starting materials.

Oxidation of $(\eta^5-C_5H_5)Zr(R)Cl$ can be accomplished using a variety of electrophilic reagents, the results of which procedures are shown in Table 1. Protic oxidizing agents such as peroxides and peracids lead directly to the alcohols; the only byproducts formed are the alkanes resulting from competing protonolysis of the C−Zr bond. For example, the functionalization, rearrangement and oxidation of 4-octene to 1-octanol can be accomplished as follows. *Cis*-4-octene (4.7 mmole) and $(\eta^5-C_5H_5)_2Zr(H)Cl$ (4.2 mmole) were stirred for 2 hrs in 12 ml benzene.[4] The solution was filtered and the amount of the octylzirconium species present was determined by nmr. *t*-Butyl hydroperoxide (5.2 mmole) was added to the yellow filtrate at room temperature. The reaction mixture became colorless and cloudy in less than 1 min, and, after stirring for several minutes more, all volatiles were removed by reduced pressure distillation. Evaporation of the solvent, byproduct octane and residual octene yielded 1-octanol (72%, based on the alkylzirconium compound, as determined by VPC).

Oxygen functions as an inexpensive and convenient, although slow, reagent to oxidize (followed by hydrolysis) $(\eta^5-C_5H_5)_2Zr(R)Cl$ to the corresponding alcohol. In many cases, yields are higher for O_2 oxidations than are found for the reagents listed in Table 1. These reactions are very clean as long as the O_2 is dried to prevent hydrolysis of the C−Zr bond. Generally, stirring a solution of the alkylzirconium(IV) complex under an atmosphere of dry O_2 for several hours is sufficient to completely consume the alkyl. For example,

TABLE 1

$$\text{Olefin} \xrightarrow[\text{2) X}]{\text{1) }(\eta^5-C_5H_5)_2Zr(H)Cl} \text{ROH}$$

Olefin	X	ROH (%)[a]	
1-octene or *cis*-4-octene	H_2O_2/NaOH(aq)	1-octanol	(69)
" "	*t*-C_4H_9OOH	"	(72)
" "	*m*-Cl-$C_6H_4CO_3H$	"	(45)
cyclohexene	H_2O_2/NaOH(aq)	cyclohexanol	(29)
"	*t*-C_4H_9OOH	"	(40)
3,3-dimethyl-1-butene	*t*-C_4H_9OOH	3,3-dimethyl-1-butanol	(59)

a. Yields were determined by VPC and are based on the alkylzirconium(IV) complex; formation of the latter occurs routinely in yields > 90% based on the olefin.[2] A slight excess of olefin was used in these experiments.

3,3-dimethyl-1-butene was oxidized to 3,3-dimethyl-1-butanol as follows. A 10% excess of the olefin was stirred with 15.1 mmole $(\eta^5-C_5H_5)_2Zr(H)Cl$ in 15 ml benzene overnight. The reaction mixture was filtered and the bright yellow solution was stirred under dry O_2.[5] Slightly less than 0.5 molar equivalent of O_2 was absorbed in 24 hrs at room temperature, 76% of which was taken up in the first hour. The resulting product was (3,3-dimethylbutoxy)-zirconium(IV) (91%)[6] from which the alcohol was obtained by hydrolysis (dil HCl). Results obtained starting with other alkenes are summarized in Table 2.

Since O_2 oxidation is the easiest way to convert these zirconium(IV) alkyls to alcohols and because the question of the mechanism of autoxidation of metal alkyls, in general, has been of interest for some time[7] (although little mechanistic information is available for autoxidation of transition metal alkyls), we have studied the mechanism of this reaction. The following points are significant in this context:

(i) Monitoring the O_2 uptake leads to a stoichiometry for the reaction of 0.5 mole O_2 per mole $(\eta^5-C_5H_5)_2Zr(R)Cl$;

(ii) After O_2 oxidation but before hydrolysis the only significant product is the Zr(IV) alkoxide, $(\eta^5-C_5H_5)_2Zr(OR)Cl$;

(iii) O_2 oxidation of a chiral alkyl complex, where R = threo- or erythro-$[(CH_3)_3CCHDCHD-]$, proceeds with approximately 50% retention and 50% racemization of configuration.[8] In contrast, oxidation of the same alkyl complex with t-C_4H_9OOH results in total retention of configuration;

(iv) $(\eta^5-C_5H_5)_2Zr(OOC_4H_9$-t$)Cl$, prepared from t-$C_4H_9OONa$ and $(\eta^5-C_5H_5)_2ZrCl_2$, reacts vigorously and rapidly with the Zr(IV) alkyl to yield equal amounts of $(\eta^5-C_5H_5)_2Zr[OC(CH_3)_3]$ and $(\eta^5-C_5H_5)_2Zr(OR)Cl$. If R is the chiral alkyl used in (iii), the reaction is observed to proceed with complete retention of configuration.

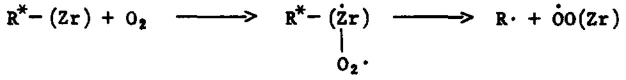
TABLE 2

$$\text{Olefin} \xrightarrow[\substack{2)\ O_2 \\ 3)\ H_3O^+}]{1)\ (\eta^5-C_5H_5)_2Zr(H)Cl} \text{ROH}$$

Olefin	ROH (%)[a]
1-octene or cis-4-octene	1-octanol (57)
cyclohexene	cyclohexanol (76)
2-methyl-2-butene	3-methyl-1-butanol (70)
1,5-hexadiene	5-hexen-1-ol (80) cyclopentylmethanol (3)
isoprene	3-methyl-3-buten-1-ol (77)

a. Yields were determined by VPC and are based on the alkylzirconium(IV) complex.

These results may be accommodated by the mechanism shown in Reaction 1. Interaction of the metal alkyl complex with O_2 induces homolysis of the C−Zr bond. The resulting alkyl radical is trapped by $(\eta^5-C_5H_5)_2Zr(Cl)OO\cdot$ to give the (racemic) (alkylperoxy)Zr(IV) complex. This, in turn, reacts rapidly with another molecule of the alkyl to yield two molecules of the Zr(IV) alkoxide, with retention of configuration for this second alkyl group. The overall stereochemical result of the reaction will thus be as observed. In further support of this mechanism we find that O_2 oxidation and subsequent hydrolysis of $(\eta^5-C_5H_5)_2Zr(5\text{-hexenyl})Cl$, formed from the hydride and 1,5-hexadiene, gives 3% cyclopentylmethanol[9] in addition to the uncyclized product, 5-hexen-1-ol (80%). A scheme analogous to Reaction 1 has been prepared for the autoxidation of Grignard[9] or lithium[7b] reagents.



$$R^*\text{–}(Zr) + O_2 \longrightarrow \underset{\displaystyle O_2\cdot}{\underset{|}{R^*\text{–}(\dot{Z}r)}} \longrightarrow R\cdot + \dot{O}O(Zr)$$

$$R\cdot + \dot{O}O(Zr) \longrightarrow ROO(Zr)$$

$$ROO(Zr) + R^*\text{–}(Zr) \longrightarrow RO(Zr) + R^*O(Zr) \qquad (1)$$

R^* = chiral alkyl R = racemic alkyl (Zr) = $(\eta^5\text{–}C_5H_5)_2Zr(Cl)\text{–}$

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REFERENCES AND NOTES

1. Part III; D. W. Hart, T. F. Blackburn, and J. Schwartz, J. Amer. Chem. Soc., 97, 679 (1975).

2. D. W. Hart and J. Schwartz, J. Amer. Chem. Soc., 96, 8115 (1974).

3. C. A. Bertelo and J. Schwartz, J. Amer. Chem. Soc., 97, 228 (1975).

4. Benzene was dried by distillation under dry N_2 from a mixture containing it, 5% tetraglyme and sodium benzophenone ketyl. The zirconium(IV) alkyls were prepared under inert atmosphere.

5. Oxygen was dried by slow passage through a 6' x 3/4" column packed with Davison Type 5A molecular sieves.

6. This product was spectrally identical to the complex prepared from 3,3-dimethylbutanol and $(\eta^5\text{–}C_5H_5)_2ZrCl_2$, and closely resembles, spectrally, analogous alkoxy complexes previously reported [D. R. Gray and C. H. Brubaker, Inorg. Chem., 10, 2143 (1971)].

7. See, for example, (a) T. G. Brilkina and V. A. Shushunov, "Reactions of Organometallic Compounds with Oxygen and Peroxides," CRC Press, Cleveland, 1969; or (b) E. J. Panek and G. M. Whitesides, J. Amer. Chem. Soc., 94, 8768 (1972), and references cited therein.

8. J. A. Labinger, D. W. Hart, W. F. Seibert III, and J. Schwartz, J. Amer. Chem. Soc., 97, 3851 (1975).

9. See C. Walling and A. Cioffari, J. Amer. Chem. Soc., 92, 6609 (1970) and references cited therein.