aromatic side chains[17] as the splitting observed between 205 and 185 nm occurs in the same spectral region as that of the peptide chromophore in an α helix,[18] the ellipticity of the CD bands being of the same order of magnitude.

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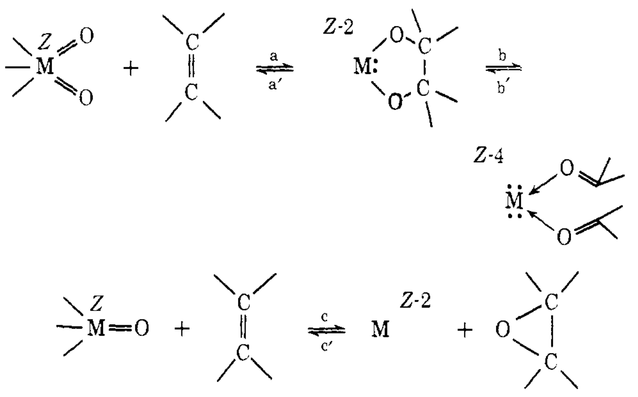
Lower Valent Tungsten Halides. A New Class of Reagents for Deoxygenation of Organic Molecules

Sir:

The transfer of oxygen from an oxotransition metal compound to an organic substrate has well-known synthetic applications such as oxygenations a, b, and c in Scheme I.[1] We have discovered a new class of reactions which involve, at least formally, the reverse processes a′, b′, and c′ (Scheme I). The reagents which effect these deoxygenations are lower valent tungsten halide derivatives. Scheme II outlines the tungsten reagents we have investigated.[2] Only K_2WCl_6 (VII) has been known previously;[3] the other reagents are new inorganic substances which we are in the process of characterizing. Although tungsten derivatives have been reported to play catalytic roles in olefin dismutation[4] and olefin epoxidation,[5] this is the first time tungsten reagents have been used stoichiometrically for organic transformations.

Scheme I. Oxygenation–Deoxygenation



Scheme II. Tungsten Reagents

$$WCl_6 + 2RLi \xrightarrow{THF} I$$

$$WCl_6 + 3RLi \xrightarrow{THF} II$$

$$WCl_6 + 4RLi \xrightarrow{THF} III$$

$$WCl_6 + 2Li \text{ dispersion} \xrightarrow{THF} IV$$

$$WCl_6 + 3LiI \xrightarrow[\textit{in vacuo}, \text{ no solvent}]{130°} V$$

$$WCl_6 + 2LiI \xrightarrow[\textit{in vacuo}, \text{ no solvent}]{130°} VI$$

$$WCl_6 + 2KI \xrightarrow[\textit{in vacuo}, \text{ no solvent}]{130°} VII^3$$

$$VII + 2LiCl \xrightarrow{THF} VIII$$

We recently described the stereoselective deoxygenation of vicinal dialkoxides to olefins (transformation a′, Scheme I) using the tetrahydrofuran insoluble reagent VII (K_2WCl_6)[6] and have since found that the soluble tungsten reagents I, II, V, and VI are also effective for this transformation. We now report the direct reductive coupling of aldehydes and ketones to olefins (formally transformation b′ + a′, Scheme I) and the stereoselective reduction of epoxides to olefins (transformation c′, Scheme I).

Rapid formation of stilbene is observed when benzaldehyde is added at room temperature to the green solution (reagent I, Scheme II) generated by addition of 2 mol of butyllithium to tungsten hexachloride (Pressure Chemical Co.) in tetrahydrofuran. There is only one precedent for this remarkable conversion; it is based on a phosphorus reagent, requires extreme conditions, and succeeds only with aromatic aldehydes.[7] Table I reveals that reagent I is also more effective for

Table I. Direct Deoxygenation of Aldehydes and Ketones to Olefins[a]

Carbonyl	Yield of olefin, %[b]	Mole of reagent I / mole of carbonyl
Benzaldehyde	76	3.8
Benzaldehyde	70	4.3
Benzaldehyde	20	1.8
p-Methoxybenzaldehyde	47	3.3
p-Methoxybenzaldehyde	38	4.1
p-Methoxybenzaldehyde	26	1.7
p-Chlorobenzaldehyde	57	3.3
m-Chlorobenzaldehyde	28	4.2
p-Cyanobenzaldehyde	20	3.9
Acetophenone	44[c]	1.9
Acetophenone	21	4.1
2-Butanone	10[d]	3.6

[a] Typically, 0.8 mmol of WCl_6 was added to 10 ml of THF cooled to −78°, followed by 1.6 mmol of butyllithium. The reaction mixture was allowed to warm to room temperature over 20 min and then the carbonyl compound (0.2 mmol) was added. After standing for 6 hr the reactions were quenched with 20% NaOH solution and extracted with ether. [b] The yields were determined by glc using internal standards. Unless noted otherwise the olefin geometry is trans. [c] The isomeric dimethylstilbenes were produced in the ratio of 60% trans and 40% cis. [d] A mixture of cis and trans isomers.

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[2] We have also prepared a number of similar reagents which reduce epoxides to olefins. These result from reaction in THF of $MoCl_5$, WCl_5, or WBr_5 with 1 equiv of butyllithium and reaction of $MoCl_5$, WBr_6, and WF_6 with 2 equiv of butyllithium. However, none of these reagents is as effective as those described in Scheme II.

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Table II. Reduction of Epoxides to Olefins[a]

Epoxide	Yield of olefin, %[b]	% retention of stereochemistry	Tungsten reagent[c]	Hr	Temp, °C[d]
trans-Cyclododecene oxide	98 (94)	95	I	2	rt
	97		IV	2.7	rt
	98		VI	2	rt
	98		VIII	2	rt
cis-Cyclododecene oxide	89	94	I	2	0
	88	96	I	2.5	−10
	70	98	I	5	−22
trans-4-Octene oxide	99	70	II[e]	2	rt
	84	>98	V	2	rt
	97	>98	II + 2LiI	0.3	rt
cis-4-Octene oxide	86	66	II[e]	2	rt
	61	80	II	1	−10
	81	93	V	2	rt
trans-Stilbene oxide	86	100	I	<0.3	rt
cis-Stilbene oxide	80	8	I	<0.3	0
Cyclooctene oxide	89		I	3	−5
1-Dodecene oxide	80		I	4.2	Reflux
	55		II	3	rt
4-Ethylcyclohexene oxide	75		I	3	Reflux
	65		II	3	rt
	47		III	3	rt
Geraniol methyl ether bisepoxide	37	72	I	1	0
Citronellol methyl ether oxide	83		I	0.3	rt
Stigmasterol acetate bisepoxide[f]	(83)[g]		II	0.3	rt

[a] Typically, 1 mmol of WCl_6 was added to 10 ml of THF cooled to −78°, followed by the alkyllithium (1.67 *M* solution). The reaction mixture was allowed to warm to room temperature over 20 min and then the epoxide (0.5 mmol) was added. Aliquots were quenched with 20% NaOH, extracted into hexane, and analyzed by glc. Reagents V and VI were simply added to tetrahydrofuran at room temperature; in all other respects the procedure was similar to that above. [b] Yields were determined either by glc using internal standards or by isolation; parentheses denote isolated yields. [c] Tungsten reagents (2 mol) were used per mole of epoxide function to be reduced. However, in the case of stigmasterol acetic bisepoxide, only 1.6 mol of reagent I was used per mole of bisepoxide. [d] rt = room temperature. [e] Use of reagent I in these two cases gave mainly chlorohydrin and only a low yield of olefin after 2 hr at room temperature. [f] Prepared in quantitative yield by treatment of stigmasterol acetate with *m*-chloroperbenzoic acid in methylene chloride. [g] The only product of this selective reduction was 22,23-epoxystigmasterol acetate. Selective peracid epoxidation of stigmasterol acetate gives the nuclear monoepoxide.

aromatic aldehydes and ketones than for simple aliphatic cases. However, the fact that it proceeds at all with saturated ketones is encouraging and suggests that a favorable mechanism exists for this type of deoxygenation. It is important to note that the coupling is specific for the carbonyl moiety, since benzal chloride, a conceivable intermediate, gave no stilbene under conditions where benzaldehyde was rapidly converted. A typical experimental procedure is identical with that described below for the use of reagent I for epoxide reduction. However, in this case the optimum ratio of tungsten reagent I to carbonyl varies between 2 and 4. In contrast to the situation for epoxide reductions, reagent I was more effective for these carbonyl couplings than were the other tetrahydrofuran-soluble tungsten reagents (II, III, IV, V, and VI, Scheme II). We are currently studying the mechanism of this unique coupling with the hope of improving the yields, especially for saturated aldehydes and ketones.

The preparation of the various tungsten reagents employed for epoxide reduction is outlined in Scheme II. Clearly, the easily prepared, prereduced solid reagents V and VI are the cheapest and most convenient reagents for these reductions; we plan to publish a detailed account of their preparation and use. However, *in situ* reduction of WCl_6 with alkyllithium in tetrahydrofuran (anhydrous ether can also be used) is a simple means of generating reagents I, II, and III for small and medium scale deoxygenations. In a typical procedure, 60 g (0.15 mol) of WCl_6 was added to 420 ml of THF (freshly distilled from sodium and benzophenone and maintained under nitrogen) cooled to −62° in a Dry Ice–acetone bath. While stirring this suspension at −62°, 31 ml (0.30 mol) of 90% *n*-butyllithium in hydrocarbon was added slowly over a 5-min period.[8a] The mixture was allowed to warm slowly to room temperature.[8b] *trans*-Cyclododecene oxide (14.8 g, 0.081 mol) was added and a rapid exothermic reduction occurred; an aliquot at 20 min revealed complete reaction. After 0.5 hr the reduction mixture was poured into 600 ml of an aqueous solution, which was 1.5 *M* in sodium tartrate and 2 *M* in NaOH, and extracted with hexane. The organic layer was dried over $MgSO_4$ and concentrated; distillation afforded 12.65 g of cyclodecene [94% yield; bp 92–98° (4.1 mm)].

A number of factors apparent in Table II deserve further comment. Monosubstituted epoxides and disubstituted epoxides in smaller rings give chlorohydrin by-products with reagent I. Chlorohydrin production can be largely suppressed by use of the less acidic reagents II, III, or V. We have good evidence that chlorohydrins are not intermediates in the normal reduction;[9] however, when they form using reagent I,

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(8) (a) This preparative reaction differs from the smaller reactions (Table II) in being 3.5 times as concentrated and in using a more concentrated solution of *n*-butyllithium. (b) A number of color changes occur; these are presumably associated with formation and decomposition of *n*-butyltungsten species. Shortly after reaching room temperature, the solution is homogeneous and deep green. The solution remains green even after the epoxide has been added and reduction is complete. It is recommended that for reactions of this scale, the epoxide be added with cooling.

(9) Under the usual reaction conditions chlorohydrins reduce much more slowly (and with complete loss of stereochemistry) than the corresponding epoxides. In these controls excess diisopropylethylamine was added to take up the HCl presumed to be formed upon alcoholysis of the tungsten reagent by the chlorohydrin. Under these conditions

they can be converted onto olefin by heating the reaction mixture at reflux. The stoichiometry of the reaction is unusual; depending on the substrate it varies from about 1.5 to 2.0 mol of I per mole of epoxide. Hence, we generally use a mole ratio of 2. Although the tungsten reagents show high stereoselectivity in reducing the isomeric cyclododecene oxides, only limited stereoselectivity is observed for reduction of acyclic disubstituted and trisubstituted epoxides. Reagent V is unique in showing high stereoselectivity even with acyclic epoxides. This is probably due to contamination by unreacted lithium iodide used in the preparation of V. Addition of lithium iodide to reagent II results in stereospecific reductions and the iodohydrin[6] can be detected in hydrolyzed aliquots of this reaction. Thus, in the presence of iodide, the process resembles mechanistically the Cornforth procedure[10] for stereospecific reduction of epoxides with the advantage that the tungsten reductions do not require separate preparation of the iodohydrin. With regard to reactivity, yield, and, in some cases, stereoselectivity (Table II), the tungsten reagents are generally superior to other reagents[11] for carrying out this same conversion in one reaction vessel.

Using only enough I to reduce one of the oxide functions, clean, selective reduction of the nuclear epoxide function of stigmasterol acetate bisepoxide was observed. We are investigating other selective reductions of polyepoxides.

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iodohydrins were rapidly and stereospecifically reduced, suggesting that the sluggishness of the reduction of chlorohydrins could not be attributed to rate-determining formation of the alkoxytungsten intermediate.

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Stereochemically Nonrigid Binuclear Acetylene Complexes of Rhodium

Sir:

Complexes of formula $Co_2(CO)_6(ac)$ and $Co_2(CO)_4(ac)_3$ have been isolated from reactions of acetylenes (ac) with dicobalt octacarbonyl.[1] We find that $Rh_2(PF_3)_8$, which resembles $Co_2(CO)_8$ in many chemical respects,[2] reacts with a variety of acetylenes (C_2H_2, $C_6H_5C_2H$, $C_6H_5C_2C_6H_5$, $CH_3C_2CH_3$, $C_6H_5C_2CH_3$, $CH_3C_2CO_2CH_3$, $n\text{-}C_4H_9C_2H$, $t\text{-}C_4H_9C_2H$, and $CF_3C_2CF_3$) to give volatile, red to yellow solids or oils of formula $Rh_2(PF_3)_6(ac)$. The structural analogy between $Rh_2(PF_3)_6(ac)$ and $Co_2(CO)_6(ac)$ has been confirmed by a three-dimensional single-crystal X-ray structural analysis of burgundy-colored $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)\cdot(C_2H_5)_2O$, obtained from $Rh_2(PF_3)_6(C_6H_5C_2C_6H_5)$ and triphenylphosphine in ether (Figure 1).

Crystal Data. triclinic space group $P\bar{1}$; $a = 21.19$ Å, $b = 12.99$ Å, $c = 12.94$ Å; $\alpha = 114.11°$, $\beta = 64.36°$, $\gamma = 115.33°$; $D_m = 1.57$, $D_c = 1.59$ (assuming 1 mol of ether per mole of complex); $Z = 2$.

The present structural determination is based on 5765 independent reflections, with $I/\sigma(I) \geqslant 6.0$, collected on a Picker FACS-I automatic diffractometer, using crystal monochromated Cu Kα radiation. With isotropic thermal parameters for all atoms, block diagonal least-squares refinement has converged to a conventional R factor of 0.091. Data have still to be corrected for absorption effects.

The molecule consists of two $Rh(PF_3)_2[P(C_6H_5)_3]$ moieties symmetrically bridged by diphenylacetylene, the C≡C bond of which is above and normal to the Rh–Rh axis; the triphenylphosphine ligands are on the same side of the molecule as the bridging acetylene. The overall geometry of the molecule is similar to those of $Co_2(CO)_6(C_6H_5C_2C_6H_5)$,[3] $Co_2(CO)_6(C_6F_6)$,[4] and related molecules,[5–8] and the Rh–Rh distance [2.741 (2) Å] indicates a metal–metal interaction [*cf.* $Rh_4(CO)_{12}$ (2.73 Å),[9] $Rh_6(CO)_{16}$ (2.78 Å),[10] and $(C_5H_5)_2Rh_2(CO)_3$ (2.68 Å)[11]]. The Rh–C distances [av 2.112 (14) Å] are equal within experimental error, and the acetylenic C–C distance [C(1)–C(2), 1.36 (2) Å] agrees well with previous values.[3–8] The Rh–PF_3 distances [av 2.216 (4) Å] are significantly shorter than the Rh–$P(C_6H_5)_3$ distances [av 2.391 (4) Å], which is consistent with the strong π-bonding ability of PF_3.

The proton resonances of the ≡CH and ≡CCH_3 groups in the appropriate $Rh_2(PF_3)_6(ac)$ complexes are downfield from those of the corresponding free acetylenes and are split into symmetrical septets by coupling to six apparently equivalent ^{31}P nuclei ($^3J_{PH} \sim 7.5$ Hz; $^4J_{P\text{-}CH_3} \sim 6.5$ Hz).

Assuming that all the $Rh_2(PF_3)_6(ac)$ complexes are structurally analogous to $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ and to $Rh_2(PF_3)_4[P(C_6H_5)_3]_2(C_6H_5C_2C_6H_5)$, it is predicted

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