Direct Deoxygenation of Vicinal Diols with Tungsten(IV). A New Olefin Synthesis

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Summary A new synthesis of olefins by the reductive deoxygenation of vicinal diols using tungsten(IV) salts is described; some mechanistic implications are discussed.

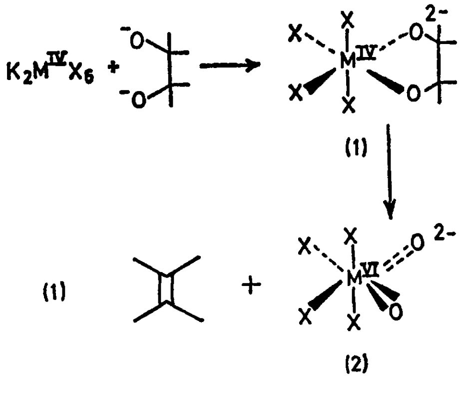
We have devised a new olefin synthesis, formally the reverse of the process involved in the reaction of permanganate or osmium tetroxide with an olefin, which involves treatment of a vicinal dialkoxide with a tungsten(IV) halide derivative in refluxing tetrahydrofuran (THF). The reaction time, yield, and stereochemistry depend markedly on substrate structure (see Table). Tetrasubstituted diols are reduced rapidly in moderate yield. Mono-, di-, and trisubstituted glycols are reduced more slowly and to lower conversion although the yields are still good. The data in the Table reveal that olefin is formed essentially by a *cis*-elimination, but some isomeric olefin is generally formed in an amount which parallels the degree of isomerization of the starting diol (*vide infra*). Unlike existing methods for the deoxygenation of vicinal diols, involving decomposition of 5-membered cyclic intermediates,[1] this reaction is easily carried out in a single reaction vessel, and thus offers a considerable increase in convenience with comparable or improved yields, particularly for the preparation of tetrasubstituted olefins, when used in conjunction with pinacolic reduction of ketones.

Table

Diol[a,b]	Olefin[b]	Yield[c]	Stereospecificity[d]	Reaction Time[e]
Docosane-1,2-diol	Docos-1-ene	44 (67)	—	2 days
cis-Cyclododecane-1,2-diol (**3**)	Cyclododecene	66 (87)	73 (91)	2 days
cis-Cyclododecane-1,2-diol[f]	Cyclododecene	36 (51)[g]	34 (27)	3 days
trans-Cyclododecane-1,2-diol (**4**)	Cyclododecene	50 (78)	92 (100)	4 days
cis-1-Methylcyclododecane-1,2-diol (**5**)	1-Methylcyclododecene	45 (71)	81 (80)	22 h
1,1′-Bicyclododecyl-1,1′-diol	1,1′-Dicyclododecenyl	74 —	—	5 h
cis-1,2-Dimethylcyclododecane-1,2-diol[h]	1,2-Dimethylcyclododecene	74 (77)	93 (100)	7 h
trans-1,2-Dimethylcyclododecene-1,2-diol[i]	1,2-Dimethylcyclododecene	72 (83)	70 (66)	9 h

[a] K_2WCl_6 (2 mol. equiv.) was added to a THF soln. of the lithium dialkoxide (prepared from diol and 2 equiv. of MeLi) under N_2; the mixture was heated under reflux and aliquot portions were taken at intervals. [b] All new compounds were characterized by spectra, mass spectra and/or elemental analysis. [c] Yields were determined by g.l.c.; the yield based on unrecovered diol is in parentheses. [d] Percentage of olefin formed by *cis*-elimination from starting diol; percentage of starting diol isomer in the recovered diol mixture is in parentheses. [e] Not necessarily optimum time. [f] 2,6-di-t-Butylpyridine was used as base in place of MeLi. [g] Cyclododecanone (30%) was formed. [h] Prepared by addition of 2-hydroxycyclododecanone to MeLi. We thank K. Nakanishi and D. A. Schooley for NOE evidence for the *cis*-stereochemistry of (**5**) which they will present in a forthcoming publication. [i] Prepared by addition of cyclododecane-1,2-dione to excess of MeLi. The relative stereochemistry of diols and products in this series is certain, but the actual stereochemical assignment is not yet unequivocal.

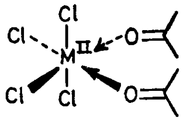
In a typical procedure, 1,2-dimethylcyclododecane-1,2-diol (9·22 mmol.) in THF (100 ml) under N_2 was converted into its dilithium salt by treatment with MeLi (2 mol. equiv.) in Et_2O, with 1,10-phenanthroline as



indicator.[2] K_2WCl_6[3] (2 mol. equiv.) was added and the heterogeneous mixture was heated under reflux for 4 h, then hydrolysed by vigorous shaking with 20% NaOH. After extraction with hexane, drying, concentration, and filtration through silica gel (pentane), the filtrate gave 1,2-dimethylcyclodecene (1·10 g, 58%) which contained *ca.* 2% of impurity (g.l.c.).

This reaction may take place by the mechanism in equation (1).[4] Dioxoate complexes such as (**2**) are well known and stable, and for Mo^{VI} and W^{VI} show a definite preference for the *cis*-configuration.[4] Because of the same O–W–O angle in (**1**) and (**2**), the stability of (**2**) can contribute directly to the stabilization of the transition state from (**1**) to (**2**).

The mechanism of equation (1) predicts a stereospecific *cis*-deoxygenation, which the data in the Table show is not entirely the case, but the following shows that this path is not ruled out by this. Schlosser recently observed the isomerization of vicinal dialkoxides when heated in solution,[5] and we have found that a *cis–trans* (18:82) equilibrium mixture is reached with 4 days in refluxing THF from either pure isomer of 1,2-dihydroxycyclododecane dilithium salt [of (**3**) or (**4**)]. To avoid this isomerization, 2,6-di-t-butylpyridine was used as the base in place of methyl-lithium. The diol would then substitute at tungsten and pyridine would trap the HCl formed, circumventing formation of the dialkoxide. Surprisingly, the amount of isomerization in both recovered diol and olefinic product increased dramatically (see Table), which suggests that isomerization of coordinated dialkoxide, which is highly dependent upon counter-ion, occurs in the tungsten(IV) intermediate (**1**). Transition state (**6**) would account reasonably for such an isomerization, and, in the reaction of $MoCl_4$ with the dialkoxide of (**3**), only dodecane-1,12-dial is formed in significant amount. Thus, while structure (**6**) is accessible for tungsten, its formation is favoured for the more strongly oxidizing molybdenum.



(6)

A second possible path involves an epoxide intermediate, formed either 'directly' from reactants, or from intermediate (**1**). Preliminary experiments show that the corresponding epoxides are in fact rapidly reduced under our reaction conditions. (In the absence of base, epoxides undergo acid-catalysed rearrangements in the presence of K_2WCl_6). There is not yet sufficient evidence to implicate or rule out an epoxide intermediate, but stereochemical evidence at this point seems against it.

The moderate conversion of less highly substituted diols into olefins is attributed to the likelihood of multiple substitution of dialkoxide on (**1**) owing to the heterogeneity of the first substitution step with the insoluble tungsten salts. The preparation of soluble lower-valent tungsten derivatives may solve this problem.

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