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Removal of α-Hydroxy Group of Acyloins and Their Derivatives with Vanadium(II)-THF Complex

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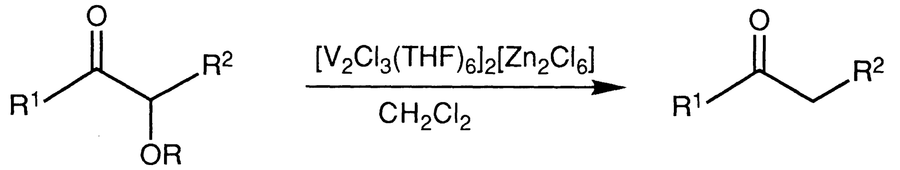
α-Hydroxy ketones (acyloins) and their acetate or mesylate derivatives were reduced to the corresponding ketones in good yields by treatment with $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ complex prepared *in situ* from $VCl_3(THF)_3$ and zinc.

The use of low valency V(II) reagent, $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$, has found great potential in the reduction of aldehydes for cross pinacol couplings.1) This V(II) reagent promoted reduction can be extended to cyclization of alkenals with high stereoselectivity.2) In addition to these carbon-carbon bond making reactions via α-oxidoalkyl radical intermediates, the V(II) reagent can be used for reduction of oxiranes to alkenes probably due to its strong oxygen affinity.3) To the best of our knowledge, however, reductive transformation of ketones by using the V(II) reagent have not been examined. Now we wish to report quick removal of α-hydroxy group of acyloin derivatives to give the corresponding ketones.4)

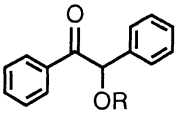
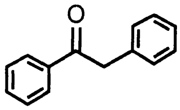
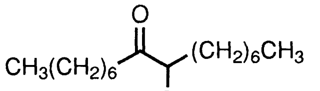
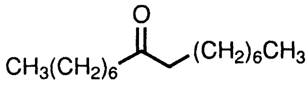
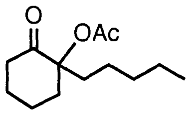
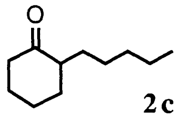
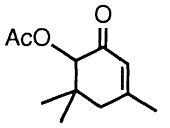
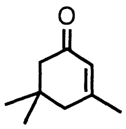
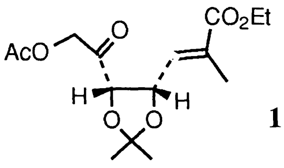
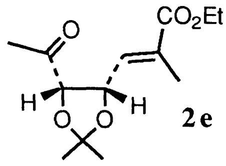


1, R = H, Ac, Ms **2**

Reduction of α-acetoxy ketones is achieved as follows. Thus, freshly prepared pink powder of $VCl_3(THF)_3$ (560 mg, 1.5 mmol) was dried in a Schlenk tube under high vacuum. Dry CH_2Cl_2 (6 ml) and zinc dust (98 mg, 1.5 mmol) were added at room temperature under a pressure of Ar. After being stirred for 30 min, a solution of benzoin acetate (**1a**, R = Ac, 182 mg, 0.75 mmol) in CH_2Cl_2 (2 ml) was added at room temperature to a stirred suspension of the V(II) reagent. The mixture was stirred for 1.75 h at the same temperature and worked up in a usual manner to give **2a** (134 mg, 91%) as crystals after purification by column chromatography (SiO_2, hexane/AcOEt = 25/1). Treatment of **1a** with one equivalent of the V(II) reagent resulted in the formation of **2a** (40%) along with the unchanged **1a** (60%). The use of three equivalent of the V(II) reagent led to completion of the reaction within 40 min (83% yield).

In a similar manner, other acetate or mesylate derivatives of α-hydroxy ketones were allowed to react with $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ complex and the results are shown in Table 1. Smooth carbon-oxygen bond cleavage at α-position is achieved by reaction of the acetate **1a** (R = Ac) and the mesylate **1a** (R = Ms) with the V(II) reagent and deoxygenation of hydroxy ketone **1a** (R = H) proceeds sluggishly compared with the acetate and the mesylate. Any destruction of the enone moiety is found in reduction of α'-acetoxylated enone **1d**. Polyfunctionalized ketone **1e** is also selectively converted to the corresponding methyl ketone **2e** without any reduction of enoate and acetal moieties. Carbon-oxygen bond of α-methylsulfonyloxyalkanoates was inert under the present conditions.

Table 1. Deoxygenation of Acyloin Derivatives with $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$[a]

Entry	Substrate	Time/h	Product	Yield/%[b]
1	 **1a**, R= Ac	1.75	 **2a**	91[c]
2	R= Ms	0.17	**2a**	80
3	R= H	43.0	**2a**	59
4	 **1b**	1.0	 **2b**	99
5	 **1c**	1.0	 **2c**	90
6	 **1d**	0.17	 **2d**	74
7	 **1e**	3.0	 **2e**	84

a) Unless otherwise noted, reactions were carried out by using 0.5-1.0 mmol of the substrate and $[V_2Cl_3(THF)_6]_2[Zn_2Cl_6]$ (three equivalents) in CH_2Cl_2 (8 ml). b) Base on isolated products. c) Carried out by using two equivalents of the V(II) reagent.

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References

1) P. M. Takahara, J. H. Freudenberger, A. W. Konradi, and S. F. Pedersen, *Tetrahedron Lett.*, **30**, 7177 (1989); J. H. Freudenberger, A. W. Konradi, and S. F. Pedersen, *J. Am. Chem. Soc.*, **111**, 8014 (1989). A. W. Konradi and S. F. Pedersen, *J. Org. Chem.*, **55**, 4506 (1990); J. Park and S. F. Pedersen, *ibid.*, **55**, 5924 (1990); A. S. Raw and S. F. Pedersen, *ibid.*, **56**, 830 (1991).
2) T. Inokuchi, H. Kawafuchi, and S. Torii, *J. Org. Chem.*, **56**, 4983 (1991).
3) T. Inokuchi, H. Kawafuchi, and S. Torii, *Synlett*, **1992**, 510.
4) A variety of methods for reduction of acyloin derivatives have been reported. Lithium diphenylphosphide: A. Leone-Bay, *J. Org. Chem.*, **51**, 2378 (1986); Pyridinium salts-$Na_2S_2O_4$: M. Wada, M. Imaoka, and T. Mukaiyama, *Chem. Lett.*, **1976**, 381; HI/AcOH: W. Reusch and R. LeMahieu, *J. Am. Chem. Soc.*, **86**, 3068 (1964); Ca/NH_3: S. Murayama, D. Chan, and M. Brown, *Tetrahedron Lett.*, **34**, 3715 (1968); J. A. Marshall and A. E. Greene, *J. Org. Chem.*, **36**, 2035 (1971); R. B. Turner, G. D. Diana, G. E. Fodor, K. Gebert, D. L. Simmons, A. S. Rao, O. Roos, and W. Wirth, *J. Am. Chem. Soc.*, **88**, 1786 (1966); $CrCl_2$: S. Danishefsky, P. Schuda, and K. Kato, *J. Org. Chem.*, **41**, 1081 (1976); L. A. Paquette, R. J. Ross, and Y.-J. Shi, *ibid.*, **55**, 1589 (1990); H. O. House and R. G. Carlson, *ibid.*, **29**, 74 (1964); $TiCl_3/LiAlH_4$ or $TiCl_4$/Zn: J. E. McMurry, M. G. Silvestri, M. P. Fleming, T. Hoz, and M. W. Grayston, *J. Org. Chem.*, **43**, 3249 (1978); SmI_2: A. B. Smith III, N. K. Dunlap, and G. A. Sulikowski, *Tetrahedron Lett.*, **29**, 439 (1988); Zn: H. Irikawa, S. Yamamura, N. Sakabe, and Y. Hirata, *ibid.*, **1967**, 553.

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