Tungsten Hexachloride (WCl_6) as a Mild and Efficient Reagent for Deprotection of Acetals and Ketals†

J. Chem. Research (S), 1998, 664–665†

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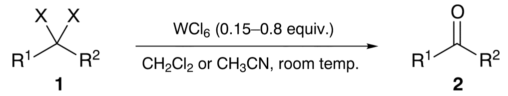
A variety of acetals and ketals are efficiently and rapidly converted to the corresponding carbonyl compounds by using WCl_6 in dichloromethane or acetonitrile at room temperature.

Acetals are one of the most useful and versatile protecting groups in organic syntheses. They find widespread application for example in the protection of carbonyl, hydroxy, and diol functions.[1] Therefore, regeneration of the parent carbonyl group from their masked form seems to be a useful synthetic process. There are several methods for the deprotection of acetals and ketals such as aqueous acid hydrolysis,[1] and K-10 montmorillonite in aqueous methanol,[2] and non-aqueous methods including those based on $TeCl_4$,[3] $[Ru(CH_3CN)_3(triphos)](OTf)_2$,[4] silica-supported guanidinium chloride–acetyl chloride,[5] $SiCl_4$–NaI,[6] K-10 montmorillonite,[7] DDQ,[8] Ph_3P–CBr_4,[9] $SnCl_2 \cdot 2H_2O$,[10] $CuSO_4$–SiO_2,[11] $CeCl_3 \cdot 7H_2O$,[12] oxidation methods[13] *etc.*[1] But the synthetic application of this transformation is so important that the introduction of improved methods continues to attract attention. New applications of tungsten hexachloride (WCl_6) have been of interest to us in recent years. Halo-dehydroxylation, dihalo-de-bisubstitution reactions and chemoselective dithioacetalization of carbonyl compounds and transthioacetalization of acetals have been reported.[14] In continuation of our studies we have found that tungsten hexachloride efficiently converts various types of acetals and ketals (dimethyl, diethyl and cyclic acetals) to the corresponding carbonyl compounds under mild reaction conditions (Scheme 1).



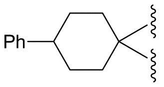
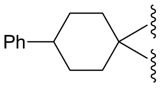
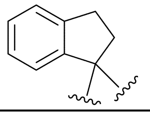
R^1, R^2 = aryl, alkyl, or H

X = OMe, OEt, XX = $-OCH_2CH_2O-$

Scheme 1

As shown in Table 1 a variety of dimethyl acetals (entry 1) and diethyl acetals (entries 2–6), of structurally different carbonyl compounds as well as 1,3-dioxolanes of aldehydes (entries 7–10) can be cleanly deprotected at room temperature using 0.15–0.2 equivalent of WCl_6 in dry CH_2Cl_2. On the other hand, cleavage of 1,3-dioxolanes derived from aromatic and aliphatic ketones was achieved in dry CH_3CN in the presence of 0.5–0.8 equivalent of WCl_6 (entries 11–16). Nitro and methoxy groups are conserved in this method (entries 5, 8). In conclusion, mild reaction conditions, easy work-up, and excellent yields of the desired products are worthy of mention as advantages of the present method.

Table 1 Deprotection of acetals and ketals with WCl_6

Entry	R^1	R^2	XX	Subst.:WCl_6 ratio	Solvent	Time/min	Yield[a] (%)
1	Ph	H	$(OMe)_2$	1:0.15	CH_2Cl_2	5	92
2	Ph	H	$(OEt)_2$	1:0.15	CH_2Cl_2	5	93
3	*p*-MeC_6H_4	H	$(OEt)_2$	1:0.15	CH_2Cl_2	3	94
4	*p*-ClC_6H_4	H	$(OEt)_2$	1:0.15	CH_2Cl_2	5	91
5	*p*-$NO_2C_6H_4$	H	$(OEt)_2$	1:0.2	CH_2Cl_2	7	98
6	 Ph		$(OEt)_2$	1:0.2	CH_2Cl_2	5	98
7	*p*-MeC_6H_4	H	$-OCH_2CH_2O-$	1:0.2	CH_2Cl_2	5	90
8	*p*-$MeOC_6H_4$	H	$-OCH_2CH_2O-$	1:0.2	CH_2Cl_2	5	89
9	PhCH=CH	H	$-OCH_2CH_2O-$	1:0.2	CH_2Cl_2	5	86
10	*n*-C_6H_{13}	H	$-OCH_2CH_2O-$	1:0.25	CH_2Cl_2	15	81
11	Ph	Me	$-OCH_2CH_2O-$	1:0.7	CH_3CN	10	94
12	*p*-ClC_6H_4	Me	$-OCH_2CH_2O-$	1:0.8	CH_3CN	10	89
13	*p*-PhC_6H_4	Me	$-OCH_2CH_2O-$	1:0.8	CH_3CN	10	82
14	$PhCH_2CH_2$	Me	$-OCH_2CH_2O-$	1:0.6	CH_3CN	10	91
15	 Ph		$-OCH_2CH_2O-$	1:0.6	CH_3CN	20	75
16			$-OCH_2CH_2O-$	1:0.8	CH_3CN	15	90

[a]The yields refer to isolated pure products.

Experimental

General Procedure for Deprotonation of Acetals with WCl_6.—To a solution of acetal **1** (2 mmol) in dry CH_2Cl_2 or CH_3CN (10 ml), WCl_6 (0.3–1.6 mmol) was added. The solution was stirred at room

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

temperature, and the progress of the reaction was monitored by TLC. On completion (3–20 min), the reaction was quenched with NaOH aqueous solution (10%; 15 ml), and extracted with CH_2Cl_2 (3 × 30 ml). The organic layer was washed successively with saturated NaCl solution (2 × 15 ml), and water (15 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave almost pure product. Further purification was achieved by column chromatography on silica gel or recrystallization from the appropriate solvent to give the desired product in good to excellent yields (Table 1).

Financial support by the Shiraz University Research Council is gratefully acknowledged.

Received, 27th May 1998; Accepted, 23rd June 1998
Paper E/8/03977A

References

1 T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis*, Wiley, New York, 1991, pp. 178–186.
2 J. Asakura, M. J. Robins, Y. Asaka and T. H. Kim, *J. Org. Chem.*, 1996, **61**, 9026.
3 H. Tani, T. Inamasu, K. Masumoto, R. Tamura, H. Shimizu and H. Suzuki, *Phosphorus, Sulfur, and Silicon*, 1992, **67**, 261.
4 S. Ma and L. M. Venanzi, *Tetrahedron Lett.*, 1993, **34**, 8071.
5 P. Gros, P. L. Perchec and J. P. Senet, *J. Chem. Res.* (*S*), 1995, 196.
6 S. S. Elmorsy, M. V. Bhatt and A. Pelter, *Tetrahedron Lett.*, 1992, **33**, 1657.
7 E. C. L. Gautier, A. E. Graham, A. McKillop, S. P. Standen and R. J. K. Taylor, *Tetrahedron Lett.*, 1997, **38**, 1881 and references cited therein.
8 K. Tanemura, T. Suzuki and T. Horaguchi, *J. Chem. Soc., Chem. Commun.*, 1992, 979; A. Oku, M. Kinugasa and T. Kamada, *Chem. Lett.*, 1993, 165.
9 C. Johnstone, W. J. Kerr and J. S. Scott, *Chem. Commun.*, 1996, 341.
10 K. L. Ford and E. J. Roskamp, *J. Org. Chem.*, 1993, **58**, 4142 and references cited therein.
11 G. M. Caballero and E. G. Gros, *Synth. Commun.*, 1995, **25**, 395.
12 E. Marcantoni, F. Nobili, G. Bartoli, M. Bosco and L. Sambri, *J. Org. Chem.*, 1997, **62**, 4183.
13 H. Firouzabadi, A. Sharifi and B. Karimi, *Iran J. Chem., Chem. Eng.*, 1993, **12**, 32 and references cited therein; H. Firouzabadi, N. Iranpoor and M. A. Zolfigol, *Bull. Chem. Soc. Jpn.*, in press; T. Nishiguchi, T. Ohosima, A. Nishida and S. Fujisaki, *J. Chem. Soc., Chem. Commun.*, 1995, 1121.
14 H. Firouzabadi and F. Shiriny, *Tetrahedron*, 1996, **52**, 14929; H. Firouzabadi, N. Iranpoor and B. Karimi, *Synlett*, 1998, 739.