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Palladium(II)-catalysed Oxidative Ring Cleavage of Cyclic Acetals with t-Butyl Hydroperoxide: Preparation of Monoesters of Diols

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Reaction of five- and six-membered cyclic acetals with ButOOH in the presence of palladium(II) catalyst gives monoesters of diols in good yields.

Cyclic acetals are important compounds for the protection of the carbonyl group,¹ and much effort has been devoted to the development of effective methods for cleaving the acetal ring. Lewis acid-induced ring opening of acetals with nucleophiles^{2,3} or halogen-induced cleavage⁴ is currently of interest. Herein we describe a novel cleavage of cyclic acetals with t-butyl hydroperoxide in the presence of palladium(II) catalyst, which affords glycol monoesters in good yields [equation (1)].[†] This is the first example of homogeneous metal-catalysed oxidation of acetals.

$$\begin{array}{c} \begin{array}{c} R \\ H \end{array} \xrightarrow{0} [CH_2]_n & \xrightarrow{Bu^{t} 00H} \\ Pd(0COCF_3)(0OBu^{t}) \end{array} \xrightarrow{R-C-O-[CH_2]_n - OH (1)} \\ \end{array} \\ \begin{array}{c} (1) \\ (1) \\ (1) \\ (2) \end{array} \\ \begin{array}{c} a; & n = 2, R = Ph \\ b; & n = 2, R = 3,4 - OCH_2OC_6H_3 - \\ c; & n = 2, R = 0 - MeC_6H_4CH_2 \\ d; & n = 2, R = C_7H_{15} \\ e; & n = 2, R = Bu^{t}C(:O)CH_2 \\ f; & n = 3, R = Ph \\ g; & n = 4, R = Ph \end{array}$$

[†] A patent claims that ozonolysis of acetals gives the same type of products; see Can. Pat., 962 264; Chem. Abs., 1975, 83, 27622e.



Table 1. Reaction of cyclic acetals with Bu^tOOH in the presence of palladium(II) catalyst.

Entry	Cyclic acetal	Reaction time/h	Product yield ^a (%)	
1	(1a)	12	68 (83) ^b	
2	(1b)	48	70	
3	(1c)	48	76	
4	(1d)	12	76 ^e	
5	(1e)	46 ^d	26	
6	(1f)	24	69°	
7	(1g)	24	38	
8	(3) ^e	12	71	
9	(4) ^f	12	78 (a:b = $67:33$) ^h	
10	(5) ^g	24	$60 (a:b = 33:67)^{h}$	

^a Isolated yield by preparative t.l.c. unless otherwise noted. ^b G.l.c. yield. ^c Isolated yield by kugelrohr distillation. ^d 10 mol% of palladium catalyst was used. ^e Compound (3) was prepared from optically active (*R*,*R*)-pentane-2,4-diol and benzaldehyde. ^t A 52:48 mixture of *cis*- and *trans*-isomers. ^g >99% *cis*-isomer. ^h Ratio of products derived from cleavage a or b.

Glycol monoesters such as those of ethylene glycol have been used as cross-linking agents for polyesters or as fungicides. The major drawback for the preparation of these compounds from diols is the concurrent formation of the diester, necessitating a tedious separation procedure.⁵ The present reaction provides a useful method for the selective mono-protection of some symmetrical diols.

The conversion of the acetal (1a) into (2a) is typical. A solution of (1a) (1 mmol) and anhydrous Bu^tOOH (benzene solution; 3.47 M; 2 mmol)⁶ in dry benzene (4 ml) was stirred at 50 °C in the presence of Pd(OCOCF₃)(OOBu^t)⁷ (0.05 mmol). The reaction was monitored by g.l.c. analysis, and after 12 h the product was taken up in ether, washed with 5 % Na₂SO₃ and brine, and dried over Na₂SO₄. Evaporation followed by preparative t.l.c. (SiO₂, benzene–EtOAc, 4:1, as eluant) gave (2a) (R_f 0.45) in 68% yield.

Other palladium(II) complexes also promote the reaction, but not as effectively as $Pd(OCOCF_3)(OOBu^t)$; the g.l.c. yields of (2a) formed under the conditions described above are as follows: with $Pd(OCOCF_3)(OOBu^t)$, 83% (12 h); $Pd(OAc)_2$, 64% (24 h); $PdCl_2$, 64% (24 h); $PdCl_2(MeCN)_2$, 62% (24 h). Even if only 1 equiv. of Bu^tOOH is used with $Pd(OCOCF_3)(OOBu^t)$ (24 h), the yield of (2a) is 79%.

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Table 1 summarizes representative results for the present reaction. Five-membered acetals (1a-d) bearing aromatic, benzylic, and alkyl substituents give the corresponding monoesters of ethylene glycol in good yields (entries 1-4). Likewise, six-membered cyclic acetals (1f) and (3) give good yields of the corresponding monoesters of propane-1,3-diols (entries 6 and 8). Thus, the reaction appears to be quite general for these types of acetals, although effective cleavage does not occur with the acetal (1e) bearing a ketone group and the seven-membered acetal (1g) (entries 5 and 7). It is noteworthy that the methylene dioxy-unit in (1b) is unaffected by this oxidation.

Five- and six-membered acetals (4) and (5) derived from unsymmetrical diols are again smoothly oxidized, but with less regioselectivity, to give the two corresponding products produced *via* cleavage of either of the two acetal C–O bonds (a or b).

A possible mechanism involves co-ordination of the acetal oxygen atom to palladium(II) followed by nucleophilic attack of Bu^tOOH on the acetal carbon atom. The Bu^tOO ligand of PdX(OOBu^t) (*e.g.*, $X = OCOCF_3$) may act as an alternative nucleophile. This process induces ring opening of the acetal with the formation of XPd-O-[CH₂]_n-CH(R)-OOBu^t. Decomposition of the peroxide species to the product and regeneration of PdX(OOBu^t) by the action of Bu^tOOH complete the catalytic cycle. The crucial step may be the co-ordination of the acetal oxygen atom to the metal, as invoked in Lewis acid-induced ring opening³ and hydrogenolytic cleavage with heterogeneous transition metal catalysts.⁸

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References

- 1 T. W. Green, 'Protecting Groups in Organic Synthesis,' Wiley-Interscience, New York, 1981; F. A. J. Meskens, Synthesis, 1981, 501.
- 2 J. M. McNamara and Y. Kishi, J. Am. Chem. Soc., 1982, 104, 7371.
- 3 P. A. Bartlett, W. S. Johnson, and J. D. Elliott, J. Am. Chem. Soc., 1983, 105, 2088; W. S. Johnson, R. Elliott, and J. D. Elliott, *ibid.*, 1983, 105, 2904.
- 4 A. Goosen and C. W. McCleland, J. Chem. Soc., Chem. Commun., 1982, 1331.
- 5 J. H. Babler and M. J. Coghlan, *Tetrahedron Lett.*, 1979, 1971, and references therein.
- 6 K. B. Sharpless and T. R. Verhoeven, Aldrichimica Acta, 1979, 12, 63.
- 7 H. Mimoun, R. Charpentier, A. Mitschler, J. Fischer, and R. Weiss, J. Am. Chem. Soc., 1980, 102, 1047.
- 8 M. Bartok and J. Czombos, J. Chem. Soc., Chem. Commun., 1981, 106.