Cleavage of Olefins by Polymer-Supported Osmium Tetroxide and Sodium Periodate

Gianfranco Cainelli,* Michele Contento, Francesco Manescalchi, Laura Plessi

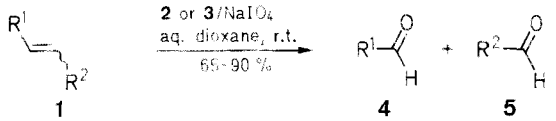
Dipartimento di Chimica "G. Ciamician", Università degli Studi di Bologna, Via F. Selmi 2, I-40126 Bologna, Italy

Oxidative cleavage of olefins has been achieved by the simultaneous use of polymer-supported osmium tetroxide and sodium periodate. Good yields of carbonyl compounds, fast reaction rate, and easy work-up are the main features of the proposed procedure.

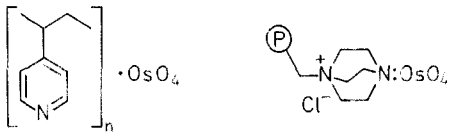
The one-pot combination of two well known reactions, namely osmium tetroxide hydroxylation of an olefin and periodate cleavage of vicinal diols, has been described[1] to afford carbonyl compounds. The continuous regeneration of osmium tetroxide by periodate allows the use of catalytic amounts of the expensive hydroxylating reagent.

In the preceding communication,[2] we reported the synthesis of 1,2-diols from alkenes by means of osmium tetroxide linked to macromolecular tertiary amines.

By adding sodium periodate to this reaction mixture we have now obtained carbonyl compounds **4** and **5** in good yields (Table).



1 4 5



2 3

Ⓟ = crosslinked styrene-divinylbenzene copolymer

1, 4, 5	R^1	R^2	1, 4, 5	R^1	R^2
a	H	n-C_8H_{17}	**f**		β-pinene
b	n-C_3H_7	n-C_3H_7	**g**	n-C_8H_{17}	n-$C_8H_{17}CO_2Et$
c	CH_3	n-C_5H_{11}	**h**	Ph	CO_2Et
d	Ph	Ph	**i**	Ph	$COCH_3$
e	$-(CH_2)_4-$				

Runs performed with catalyst **2** have been omitted as they were too time-consuming and required a high percentage of active osmium tetroxide to attain a good yield. In contrast, catalyst **3** proved to be much more effective giving good to excellent yields of products sometimes even within an hour. In this case the ionic nature of the polymeric matrix probably provides more favorable conditions for the diffusion of reactants into the resin.[3]

A remarkable feature, enhancing the molar ratio substrate/catalyst and increasing the reaction scale is provided by the possibility of repeating many times the double bond cleavage by adding successively, in the same vessel, soon after the end of a run, a new portion of olefin and periodate. The process was carried out for ten times without any decrease in efficiency.

In conclusion, due to the facility and safety of performance, our method seems to represent a valuable alternative to the double bond cleavage by ozone.

Table. Oxidative Cleavage of Olefins **1** by Catalyst **3** and Sodium Periodate

Substrate	Reaction Conditions[a] Temp (°C)/ Time (h)	Product[b]	Yield[c] (%)	mp (°C)[d] bp (°C)/ Torr	Lit. mp (°C) or bp (°C)/Torr
1a	r.t./0.5	nonanal	77[e] (100)	96	96[4]
1b	r.t./2	butanal	90[e]	122	122[4]
1c	r.t./2	hexanal	75[e] (99)	103	104[4]
1d	r.t./1	benzaldehyde	73[e]	238–240	240–241[1]
1e	r.t./1	hexandial	65[e]	231–233	234–235[1]
1f	83[f]/2.5	nopinone	83	50–51/2	50–51/2[5]
1g	r.t./5	ethyl 8-oxo-octanoate + nonanal	70[g]	150–153/12	151–154/12[6]
1h	r.t./2	benzaldehyde	85[e] (100)	–[e]	–
1i	r.t./2	benzaldehyde	80[e] (100)	–[e]	–

[a] In 75% aqueous dioxane (acetone and THF are also suitable) with **3** (0.5–1% of OsO_4), and $NaIO_4$ (4-fold excess).
[b] Only preparatively relevant products are reported.
[c] GC yields are given in parenthesis.
[d] mp Values (uncorrected, measured with a Büchi 510 apparatus) refer to 2,4-dinitrophenylhydrazones.
[e] Isolated and identified as 2,4-dinitrophenylhydrazones.
[f] In *tert*-butyl alcohol at reflux, in the presence of molar quantities of trimethylamine *N*-oxide.
[g] Refers to yield of ethyl 8-oxooctanoate, isolated by flash chromatography (eluent: hexane/EtOAc, 4:1), and identified by IR and ^{1}H-NMR spectra.

As previously described,[2] OsO_4 can be easily complexed either on poly-4-vinylpyridine crosslinked (Reilly Co.), catalyst **2**, or over a resin obtained by quaternization of 1,4-diazabicyclo[2.2.2]octane (DABCO) with chloromethylated styrene-divinylbenzene copolymer (capacity 4 mequiv/g, Rohm and Haas Co.), catalyst **3**.

Reactions are carried out on 1–3 mmol scale of olefin at room temperature in the presence of 0.5–1% of polymer-supported OsO_4. Aqueous dioxane (75%, acetone and THF are also suitable) is used as solvent and $NaIO_4$ is added in 3 to 4-fold excess.

Oxidative Cleavage of (*E*)-4-Octene; Typical Procedure:
A 50 mL one-necked flask is charged with dioxane (15 mL), water (3 mL), (*E*)-4-octene (**1b**; 0.36 g, 3.2 mmol) and catalyst **3** (0.15 g, about 0.03 mmol of active hydroxylating reagent). To the well-stirred mixture, finely powdered $NaIO_4$ (2.5 g, 11.4 mmol) is added in portions keeping the temperature below 20°C. The reaction is monitored by GC, and after 2 h, the alkene is completely consumed. The resin is filtered, and the filtrate is extracted with ether (200 mL). The dried (Na_2SO_4) ether solution is treated with a solution of 2,4-dinitrophenylhydrazine (1.4 g) in conc. H_2SO_4 (7 mL), water (11 mL), EtOH (50 mL), and stirred for 1 h. By reducing the volume to 50 mL, the yellow 2,4-dinitrophenylhydrazone of butanal (**4b** ≡ **5b**) is obtained; yield: 1.47 g (90%); mp 122°C (CH_3OH) (Lit.[4] mp 122°C).

Received: 21 June 1988; revised: 12 September 1988

(1) Pappo, R., Allen, D.S., Jr, Lemieux, R.U., Johnson, W.S. *J. Org. Chem.* **1956**, *21*, 478.
(2) Cainelli, G., Contento, M., Manescalchi, F., Plessi, L. *Synthesis* **1989**, 45.
(3) Cainelli, G., Contento, M., Manescalchi, F., Plessi, L. *J. Chem. Soc. Chem. Commun.* **1982**, 725.
(4) Allen, C.F.H. *J. Am. Chem. Soc.* **1930**, *52*, 2957.
(5) Grimshaw, J., Grimshaw, J.T., Juneja, H.R. *J. Chem. Soc. Perkin Trans. 1* **1972**, 50.
(6) *Beilstein 1* (III), 248.