Catalytic Hydroxylation of Olefins by Polymer-Bound Osmium Tetroxide

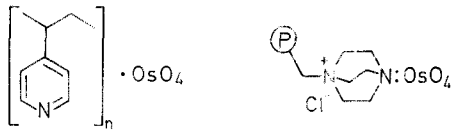
Gianfranco Cainelli,* Michele Contento, Francesco Manescalchi, Laura Plessi

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

Osmium tetroxide, linked to insoluble crosslinked polymers and copolymers bearing tertiary amino functions, has been used in the presence of secondary oxidants, such as hydrogen peroxide, *tert*-butyl hydroperoxide and trimethylamine *N*-oxide, to accomplish the catalytic hydroxylation of olefins. The polymeric reagent offers the advantages of easy and safe handling, and simple separation from the reaction medium. Generally good yields of vicinal diols have been obtained.

Osmium tetroxide has long been known as the reagent of choice to convert alkenes to *cis* diols,[1] usually in the presence of tertiary amines such as pyridine, which dramatically increase[2] the rate of reaction. Hazardous toxicity and high cost are the chief drawbacks in the use of osmium tetroxide: the first has been overcome by the use of several stable and nonvolatile adducts with tertiary amines, which retain the original character of the reagent,[3] the latter by the development of alternative procedures, where catalytic amounts of osmium tetroxide are joined with a secondary oxidant continuously regenerating the tetroxide,[4] added in stoichiometric ratio to the substrate.

Now we report on the results obtained in the hydroxylation of olefins **3** using osmium tetroxide linked to macromolecular insoluble tertiary amines. Several polymers have been employed for this purpose beginning with crosslinked poly-4-vinylpyridine (Reilly 8050 from Reilly Co.) due to its obvious analogy to pyridine. Besides this commercially available resin, different anchoring polymers have been prepared by quaternization of tertiary amines, e.g., 1,4-diazabicyclo[2.2.2]octane (DABCO),

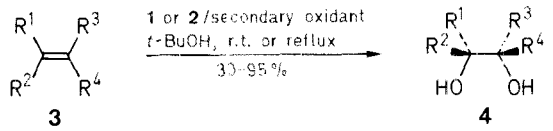


1 **2**

Ⓟ = crosslinked styrene-divinylbenzene copolymer

hexamethylenetetramine, *N,N,N',N'*-tetramethylethylenediamine with chloromethylated styrene divinylbenzene copolymers.

Each of the above mentioned polymers was charged with osmium tetroxide by stirring a weighed sample of resin in a cyclohexane solution of a known amount of the reagent. Reactions, performed with simple alkenes as well as functionalized ones, were carried out on 5–10 mmol scale, usually in *tert*-butyl alcohol as solvent, in the presence of 0.2–1% of polymer supported osmium tetroxide. Hydrogen peroxide,[5] *tert*-butyl hydroperoxide (*t*-BuOOH)[6] at room temperature, and trimethylamine *N*-oxide[7] in refluxing *tert*-butyl alcohol were tried as secondary oxidants (Table).

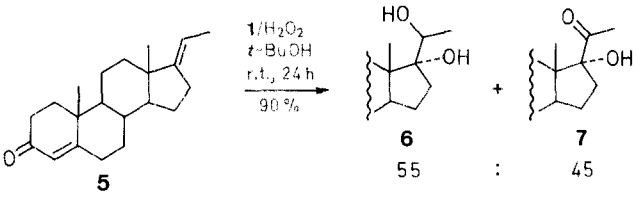


3 4

3, 4	R^1	R^2	R^3	R^4
a	H	H	H	n-C_8H_{17}
b	CH_3	H	H	n-C_5H_{11}
c		cyclooctene		
d	Ph	H	H	Ph
e	CH_3	CH_3	CH_3	CH_3
f		β-pinene		
g	n-C_8H_{17}	H	n-$C_4H_{17}CO_2Et$	H
h	Ph	H	H	CO_2Et
i	CO_2Et	H	H	CO_2Et
j	CO_2Et	H	CO_2Et	H
k	CH_3	CH_3	H	$COCH_3$
l	H	H	CH_3	$CH(OH)C_4H_9$-n

Concerning the behavior of the supports prepared from chloromethylated styrene–divinylbenzene copolymer, their efficiency was practically the same, no matter their capacity or the nature of the tertiary amine linked to the macromolecular backbone.

Hydrogen peroxide, used as secondary oxidant in the case of the stereoidical substrate **5** produced, as often happens with this reagent,[4] a noticeable amount of overoxidation product, the ketol **7** beside the expected product **6**. *tert*-Butyl hydroperoxide, under alkaline conditions,[6] gave medium to good yields of diols and proved to be the reagent of choice in the case of hindered olefins and of substrates with polar groups. In this context reagent **2** gave faster reaction rates than **1** perhaps as a consequence of selectivity effects due to the polarity of the polymeric matrix.[8] The best results, fast reaction rate, and high yields in the hydroxylation of hydrocarbon substrates were attained by means of trimethylamine *N*-oxide in conjunction with either **1** or **2**.



5 6 : 7
55 : 45

The use of polymer-supported osmium tetroxide provides the advantage of an easy work-up as there is no need of decomposition of the residual osmium tetroxide in the reaction medium.

The macromolecular nitrido complex of osmium tetroxide, stored in a bottle without any particular care, proved to be stable for several weeks. After standing for six months, however, even in tightly stoppered flask, the reagent was somewhat less active. In conclusion, the method of hydroxylating olefins by means of polymer-supported osmium tetroxide provides some attractive features. Functionalized resins, prepared from chloromethylated styrene–divinylbenzene copolymers, generally appear to be more effective than crosslinked poly-4-vinylpyridine. Among the secondary oxidants, trimethylamine *N*-oxide gives in several cases fast reaction and excellent yields.

Table. Vicinal Diols **4** from Olefins **3** by Catalysts **1** or **2**

Product	Reaction Conditions: Catalyst/Cooxidant	Temp. (°C)/Time (h)	Yield[a] (%)	mp (°C) bp (°C)/Torr	Molecular Formula[b] Lit. mp(°C), bp(°C)/Torr
4a	**1**/*t*-BuOOH	r.t./96	45	45–46	48–49[10]
	2/*t*-BuOOH	r.t./48	75		
	1/$Me_3N{\rightarrow}O$	83/0.5	90		
	2/$Me_3N{\rightarrow}O$	83/0.5	95		
4b	**1**/$Me_3N{\rightarrow}O$	83/17	80	115–17/12	$C_8H_{18}O_2$[c] (146.0)
	2/$Me_3N{\rightarrow}O$	83/0.5	90		
4c	**2**/*t*-BuOOH	r.t./36	68	76–77	77.5–79[11]
	2/$Me_3N{\rightarrow}O$	83/0.5	90		
4d	**2**/$Me_3N{\rightarrow}O$	83/0.5	80	137–38	137–38[12]
4e	**2**/*t*-BuOOH	r.t./60	50	40–41	41–43[8]
	2/$Me_3N{\rightarrow}O$	83/6	30		
4f	**2**/$Me_3N{\rightarrow}O$	83/1	82	83–84	84–85.5[13]
4g	**1**/$Me_3N{\rightarrow}O$	83/5	90	99–100	99–100[14]
	2/*t*-BuOOH	r.t./60	60		
	2/$Me_3N{\rightarrow}O$	83/7	85		
4h	**2**/*t*-BuOOH	r.t./48	70	181–83/0.2	180/0.2[15]
4i	**2**/*t*-BuOOH	r.t./60	95	130–32/12	157–59/18[5]
4j	**2**/*t*-BuOOH	r.t./60	60	51–53	53–54[5]
4k	**2**/*t*-BuOOH	r.t./60	45	102–105/12	104–110/16[5]
4l	**1**/*t*-BuOOH	r.t./24	35	138–40/12	$C_8H_{18}O_3$[d] (162.0)
6 + **7**	**1**/H_2O_2	r.t./24	90	**6**: 196–198 **7**: 219–220	201–204[16] 222–223[17]

[a] Yields refer to pure isolated compounds. All known compounds are characterized by IR and ^{1}H-NMR data.

[b] Satisfactory microanalyses obtained: C ±0.06, H ±0.05.

[c] ^{1}H-NMR ($CDCl_3$/TMS): δ = 0.85 (t, 3H, *J* = 5 Hz); 1.17 (d, 3H, *J* = 6 Hz); 1.4 (m, 8H); 3.2–3.7 (m, 4H) (Varian EM 390 spectrometer). MS (70 eV): *m/z* = 55 (100%) (double focusing Varian MAT 112 spectrometer).

[d] ^{1}H-NMR (acetone-d_6/TMS): δ = 1 (t, 3H, *J* = 5 Hz); 1.15 (s, 3H); 1.2–1.7 (m, 6H); 3.5 (m, 3H); 3.8 (br s, 3H). MS (70 eV): *m/z* = 43 (100%).

Anchoring polymers are prepared starting from chloromethylated styrene–divinylbenzene copolymers of either 1 mequiv Cl/g (from Aldrich) or 4 mequiv Cl/g (from Rohm and Haas Co.) capacity. These resins are stirred for 24 h in refluxing $CHCl_3$, with tertiary amines chosen among those known from the literature[3] to give stable adducts with OsO_4. DABCO, hexamethylenetetramine, *N,N,N',N'*-tetramethylethylenediamine. The polymers are filtered off, washed with $CHCl_3$, acetone and ether, and dried under vacuum at room temperature overnight. Nitrogen elemental analysis and chloride ion titration[9] give a value of 80–90% of quaternization.

Preparation of Polymer-Bound Osmium Tetroxide:
To a sample of resin (2 g) in cyclohexane (5 mL) is added, under an inert atmosphere, a solution of OsO_4 (0.1 g) in cyclohexane (10 mL). After stirring overnight at room temperature, the polymer is filtered off, washed with cyclohexane (20 mL in portions), and dried under vacuum. Iodometric tests on solvent and washings are negative leading us to conclude that the whole amount of OsO_4 in solution has been complexed, polymers now bearing 0.05 g (0.195 mmol) of the reagent per gram.

Preparation of 1,2-Decanediol (4a) by Oxidation of 3a with Catalysts 1 or 2/*tert*-Butyl Hydroperoxide; Typical Procedure:
A 50 mL one-necked flask is charged with *tert*-butyl alcohol (5 mL), 10% aq. Et_4NOH (1.5 mL, ca. 1 mmol), 1-decene (**3a**; 1.4 g, 10 mmol) and catalyst **1** or **2** (0.1 g, ca. 0.02 mmol of active hydroxylating reagent). The mixture is cooled to 0°C in an ice-salt bath, and 70% aq. *t*-BuOOH (2 mL, 16 mmol) is added in one portion. The temperature is allowed to rise to 20°C, and the reaction is monitored by GC. After 2 d an additional quantity of *t*-BuOOH (2 mL) is added to complete the reaction. The resin is filtered and washed with CH_2Cl_2 (10 mL). Some water can be removed in a separatory funnel, and the organic layer is dried (Na_2SO_4). The solution is evaporated, and the crude product is purified by flash chromatography (eluent: EtOAc) to give 1,2-decanediol **(4a)** as a white solid; yield: 0.78 g, (45% using catalyst **1**) and 1.3 g (75% using catalyst **2**); mp 45–46°C (Lit.[10] mp 48–49°C); identified by comparison with an authentic sample and by IR, ^{1}H-NMR, and MS.

Preparation of 1,2-Cyclooctanediol (4c) by Oxidation of 3c with Catalysts 1 or 2/Trimethylamine *N*-oxide; Typical Procedure:
A 50 mL one-necked flask is charged with *tert*-butyl alcohol (10 mL), water (3 mL), cyclooctene (**3c**; 0.55 g, 5 mmol), trimethylamine *N*-oxide (0.75 g, 6.8 mmol) and **1** or **2** (0.05 g, ca. 0.01 mmol). The mixture is stirred at reflux, and the reaction, monitored by GC, is complete in 0.5 h. After cooling, the resin is filtered and washed with CH_2Cl_2 (10 mL). Water is removed in a separatory funnel, and the organic layer is dried (Na_2SO_4). The solvent is evaporated, and the crude product is purified by flash chromatography (eluent: EtOAc) to afford 1,2-cyclooctanediol **(4c)** as a white solid; yield: 0.57 g (80%, using catalyst **1**) and 0.64 g (90% using catalyst **2**); mp 75–76°C (Lit.[11] mp 77.5–79°C) identified by comparison with an authentic sample and by IR, ^{1}H-NMR, and MS.

Received: 21 June 1988; revised: 12 September 1988

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